# Supporting Information

# Synthesis and Isolation of Less Stable Cyclopropene-1-Carboxylates

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## 1. General information

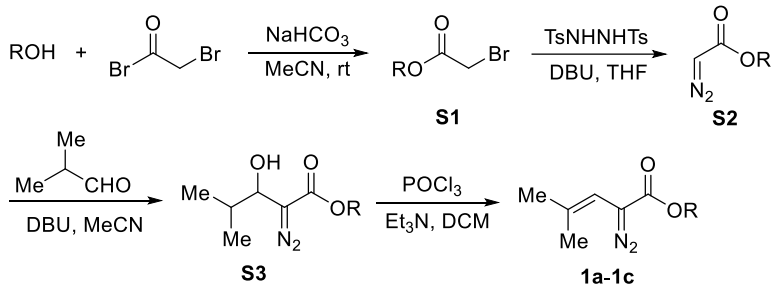
Unless otherwise noted, all commercially available compounds and analytic pure grade solvents were used as provided without further purification. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.5 mm) or Sorbent Silica Gel 60 F254 plates. For column chromatography, 200-300 mesh silica gel (Qingdao, China) were used. High-resolution mass spectra (HRMS) were performed on ThermoFisher Q Exactive using orbitrap as the mass analyser with atmospheric pressure chemical ionization (APCI) source or electrospray ionization (ESI) source. UV-Vis absorbance spectra were recorded on Shimadzu UV-2700 UV-Vis spectrophotometer. $^{1}H$ and $^{13}C$ NMR spectra were recorded on Brucker ARX 400 spectrometer or Brucker ARX 600 spectrometer in $CDCl_3$, DMSO-*d*6, $CD_3OD$. Chemical shifts for $^{1}H$ NMR spectra were reported in ppm downfield from TMS with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm; DMSO-*d*6: δ 2.50 ppm; $CD_3OD$: δ 3.31 ppm). Chemical shifts for $^{13}C$ NMR spectra were reported in ppm downfield from TMS with the solvent as the internal standard ($CDCl_3$: δ 77.16 ppm), and *J* values were given in Hz. The letters s, d, t, q and m are used to indicate a singlet, doublet, triplet, quadruplet, and multiplet, respectively.

## 2. Preparation of vinyldiazo compounds

All the vinyldiazo compounds were prepared according to the known methods.[1-5] Except for **1d**,[6] other vinyldiazo compounds are new. They are stable in a -18 °C freezer and can be stored for about two weeks.

***Caution***: To the best of our knowledge, the relevant safety studies have not been carried out on vinyldiazo compounds. However, diazo compounds are potentially explosive, and therefore must be handled with caution. They are also toxic and prone to cause development of specific sensitivity. We recommend that all operations be carried out in a well-ventilated hood behind a blast shield.

### 2.1 Preparation of vinyldiazo compounds 1a-1c.[1-4]



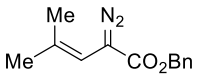

***Synthesis of S1:*** A solution of alcohol (10 mmol) and $NaHCO_3$ (30 mmol, 3.0 equiv.) in acetonitrile (30 mL) was cooled to 0 °C. Bromoacetyl bromide (15 mmol, 1.5 equiv.) was added dropwise via syringe over 10 minutes. The reaction mixture was maintained at 0 °C with vigorous stirring for 30 minutes, then quenched with water (20 mL). The aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic phases were washed with saturated brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to yield the crude bromoacetate which was used in the next step without purification.

***Synthesis of S2:*** The bromoacetate product **S1** and *N,N′*-ditosylhydrazine (2 equiv.) were dissolved in THF (50 mL), and cooled to 0 °C. 1,8-Diazabicycloundec-7-ene (DBU, 5.0 equiv.) was added dropwise over 15 minutes while maintaining the temperature at 0 °C. The resulting solution was stirred for 45-60 minutes at 0 °C, then quenched with saturated $NaHCO_3$ (30 mL) and extracted with $Et_2O$ (3 × 30 mL). The combined organic phases were washed with saturated brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to yield the crude diazo compound which was purified on a silica column using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to give desired diazoacetate as a pale-yellow oil.

***Synthesis of S3:*** DBU (1 equiv.) was added to a solution of **S2**, isobutyraldehyde (1.2 equiv.) in MeCN (20.0 mL) at room temperature. The mixture was stirred until consumption of the starting material (typically 6 to 12 h) as monitored by TLC. After completed the reaction, the solvent was removed under reduced pressure, and the residue was purified on a silica column using petroleum ether/ethyl acetate (5:1, v/v) as the eluent to give the desired β-hydroxy-α-diazo carbonyl product as yellow oil.

***Synthesis of 1a-1c:*** To a solution of **S3** and $Et_3N$ (4.0 equiv.) in $CH_2Cl_2$ (0.33 M) at 0 °C was slowly added a solution of $POCl_3$ (1.5 equiv.) in $CH_2Cl_2$ over 20 minutes. The resulting solution was warmed to room temperature and stirred for 2 h. The solution was washed with water and dried over anhydrous $Na_2SO_4$. The crude product was purified on a silica column using petroleum ether/ethyl acetate (100:1, v/v) as the eluent to give desired vinyldiazo compounds as red oil.

**benzyl 2-diazo-4-methylpent-3-enoate (1a)**



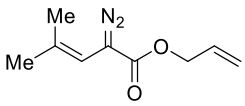

Red oil. (1.522 g, 66% yield over four steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.28 (m, 5H), 5.43 (s, 1H), 5.24 (s, 2H), 1.86 (s, 3H), 1.68 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 136.1, 135.8, 128.6, 128.3, 128.2, 106.4, 66.6, 26.2, 19.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2O_2$ 231.1128; Found 231.1122.

**allyl 2-diazo-4-methylpent-3-enoate (1b)**



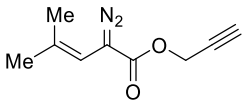

Red oil. (0.996 g, 55% yield over four steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 6.03 – 5.86 (m, 1H), 5.42 (s, 1H), 5.32 (d, $J$ = 17.2 Hz, 1H), 5.24 (d, $J$ = 10.4 Hz, 1H), 4.69 (d, $J$ = 5.7 Hz, 2H), 1.86 (s, 3H), 1.68 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 166.7, 135.8, 132.3, 118.2, 106.4, 65.5, 26.1, 19.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{13}N_2O_2$ 181.0972; Found 181.0966.

**prop-2-yn-1-yl 2-diazo-4-methylpent-3-enoate (1c)**



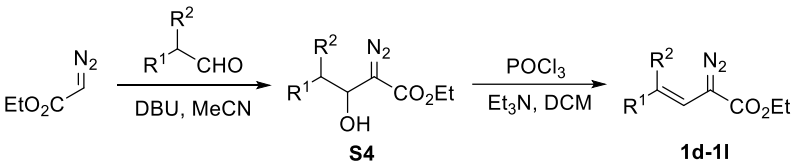
Red oil. (0.839 g, 47% yield over four steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.42 (s, 1H), 4.79 (d, *J* = 2.4 Hz, 2H), 2.48 (t, *J* = 2.5 Hz, 1H), 1.86 (s, 3H), 1.68 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 166.1, 136.4, 106.0, 77.7, 75.0, 52.3, 26.1, 19.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{11}N_2O_2$ 179.0815; Found 179.0813.

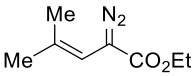
**2.2 Preparation of vinyldiazo compounds 1d-1l**.[5]




***Synthesis of S4:*** DBU (10 mmol, 1 equiv.) was added to a solution of ethyl diazoacetate (12 mmol, 1.2 equiv.), aldehyde (10 mmol, 1 equiv.) in MeCN (20.0 mL) at room temperature. The mixture was stirred until consumption of the starting material (typically 6 to 12 h) monitored by TLC. After completed the reaction, the solvent was removed under reduced pressure, and the residue was purified on a silica column using ethyl acetate/hexanes (20:80, v/v) as the eluent to give the desired β-hydroxy-α-diazo carbonyl product as yellow oil.

***Synthesis of 1d-1l:*** To a solution of **S4** and $Et_3N$ (4.0 equiv.) in $CH_2Cl_2$ (0.33 M) at 0 °C was slowly added a solution of $POCl_3$ (1.5 equiv.) in $CH_2Cl_2$ over 20 minutes. The resulting solution was warmed to room temperature and stirred for 2 h. The solution was washed with water and dried over anhydrous $Na_2SO_4$. The crude product was purified on a silica column using ethyl acetate/hexanes (1:80, v/v) as the eluent to give the desired γ,γ-disubstituted vinyldiazoacetates as red oil.

**ethyl 3,3-dimethylcycloprop-1-ene-1-carboxylate (1d)**[5]

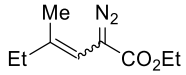


Red oil. (1.293 g, 70% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.43 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.88 (s, 3H), 1.70 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 167.0, 135.4, 106.5, 61.0, 26.1, 19.1, 14.5.

**ethyl-2-diazo-4-methylhex-3-enoate (1e)**



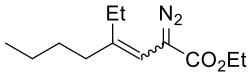

Red oil. (1.315 g, 72% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v). Mixture of *E*- and *Z*- isomers (*E*/*Z* = 3:1);

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.43 – 5.37 (m, 0.69H), 5.38 – 5.37 (m, 0.23H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.15 (q, *J* = 7.5 Hz, 1.51H), 2.05 (q, *J* = 7.8 Hz, 0.54H), 1.84 (d, *J* = 1.4 Hz, 0.75H), 1.67 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 2.25H), 1.00 (t, *J* = 7.6 Hz, 0.75H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 167.1, 140.8, 140.3, 105.8, 105.2, 61.0, 32.8, 26.0, 23.3, 17.4, 14.5, 12.6, 12.1.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{15}N_2O_2$ 183.1128; Found 183.1127.

**ethyl-2-diazo-4-ethyloct-3-enoate (1f)** [5]



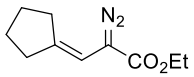

Red oil. (1.712 g, 76% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v). Mixture of *E*- and *Z*- isomers (*E*/*Z* = 2:1)

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.36 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.18 – 2.10 (m, 2H), 2.08 – 1.98 (m, 2H), 1.47 – 1.37 (m, 1H), 1.36 – 1.25 (m, 6H), 1.05 (t, *J* = 7.4 Hz, 1H), 0.99 (t, *J* = 7.6 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 167.1, 144.4, 144.3, 105.3, 104.8, 61.1, 36.8, 31.0, 30.4, 30.3, 30.3, 24.1, 23.0, 22.5, 14.5, 14.0, 14.0, 12.8, 12.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{21}N_2O_2$ 225.1598; Found 225.1598.

**ethyl 3-cyclopentylidene-2-diazopropanoate (1g)**



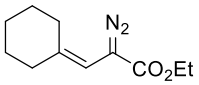

Red oil. (1.368 g, 70% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.50 – 5.46 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.45 – 2.38 (m, 2H), 2.18 – 2.10 (m, 2H), 1.73 (p, *J* = 6.8 Hz, 2H), 1.62 (p, *J* = 6.2 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 166.9, 144.2, 101.7, 61.1, 35.0, 29.2, 26.6, 26.1, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}N_2O_2$ 195.1128; Found 195.1126.

**ethyl 3-cyclohexylidene-2-diazopropanoate (1h)**



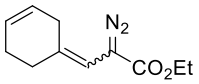

Red oil. (1.526 g, 73% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.36 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.23 – 2.19 (m, 2H), 2.13 – 2.05 (m, 2H), 1.60 – 1.50 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 167.1, 143.4, 103.4, 61.0, 36.9, 29.7, 28.0, 27.0, 26.1, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}N_2O_2$ 209.1285; Found 209.1282.

**ethyl-3-(cyclohex-3-en-1-ylidene)-2-diazopropanoate (1i)**




Red oil. (1.278 g, 62% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

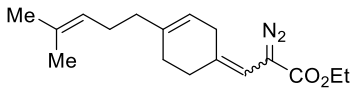
Mixture of *E*- and *Z*- isomers (*E*/*Z* = 3:1);

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.82 – 5.57 (m, 2H), 5.53 (s, 0.22H), 5.46 (s, 0.68H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.89 – 2.84 (m, 0.50H), 2.72 – 2.65 (m, 1.52H), 2.39 (t, *J* = 6.4 Hz, 1.52H), 2.30 (t, *J* = 6.4 Hz, 0.50H), 2.21 – 2.11 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ166.8, 139.3, 138.1, 127.4, 126.6, 126.1, 124.4, 104.9, 104.4, 61.1, 35.1, 32.6, 29.1, 26.4, 26.33, 26.28, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}N_2O_2$ 207.1128; Found 207.1123.

**ethyl-2-diazo-3-(4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-ylidene)propanoate (1j)**




Red oil. (2.372 g, 82% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

Mixture of *E*- and *Z*- isomers (*E*/*Z* = 2:1)

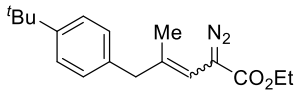
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 5.51 (s, 0.51H), 5.48 – 5.43 (m, 0.80H), 5.40 – 5.35 (m, 0.19H), 5.34 – 5.29 (m, 0.46H), 5.15 – 5.03 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.88 – 2.83 (m, 0.32H), 2.81 – 2.76 (m, 0.30H), 2.72 – 2.63 (m, 1H), 2.62 – 2.55 (m, 0.43fH), 2.39 (t, *J* = 6.4 Hz, 1H), 2.36 – 2.21 (m, 1H), 2.18 – 2.02 (m, 4H), 2.01 – 1.91 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 166.9, 166.7, 139.8, 139.6, 138.9, 138.3, 138.2, 137.5, 137.0, 135.2,

131.6, 131.4, 124.13, 124.05, 121.2, 120.2, 119.5, 117.9, 104.44, 104.36, 104.0, 61.0, 38.4, 37.6, 37.2, 37.1, 35.0, 32.9, 32.7, 32.2, 29.6, 29.4, 28.9, 26.4, 26.3, 26.2, 26.0, 25.6, 17.6, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}N_2O_2$ 289.1911; Found 289.1905.

**ethyl-5-(4-(tert-butyl)phenyl)-2-diazo-4-methylpent-3-enoate (1k)**



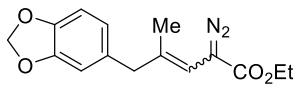

Red oil. (2.426 g, 81% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v). Mixture of *E*- and *Z*- isomers (*E*/*Z* = 7:1)

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.36 – 7.28 (m, 2H), 7.15 – 7.09 (m, 1.75H), 7.08 – 7.04 (m, 0.25H), 5.62 (s, 0.13H), 5.55 (s, 0.87H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 1.75H), 3.36 (s, 0.25H), 1.78 (s, 0.40H), 1.63 (s, 2.60H), 1.31 (s, 9H), 1.29 (t, 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 166.9, 149.2, 137.8, 137.2, 136.0, 135.2, 128.5, 128.1, 125.4, 125.3, 108.0, 61.1, 45.9, 38.3, 34.4, 31.4, 24.1, 17.2, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}N_2O_2$ 301.1911; Found 301.1904.

**ethyl-5-(benzo[d][1,3]dioxol-5-yl)-2-diazo-4-methylpent-3-enoate (1l)**



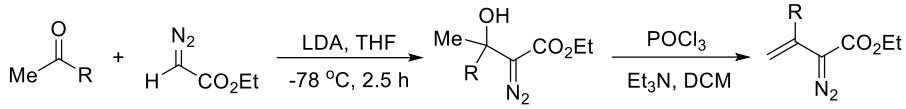

Red oil. (2.379 g, 82% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v). Mixture of *E*- and *Z*- isomers (E/Z = 7:1)

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 6.76 – 6.71 (m, 1H), 6.68 – 6.56 (m, 2H), 5.93 (s, 2H), 5.62 – 5.59 (m, 0.13H), 5.55 – 5.50 (m, 0.85H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 1.73H), 3.30 (s, 0.26H), 1.76 (d, *J* = 1.4 Hz, 0.40H), 1.60 (d, *J* = 1.3 Hz, 2.60H), 1.29 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 166.8, 147.7, 146.1, 137.5, 136.9, 132.9, 132.0, 121.8, 121.3, 109.2, 108.8, 108.2, 100.9, 61.1, 46.1, 38.4, 23.9, 17.0, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}N_2O_4$ 289.1183; Found 289.1176.

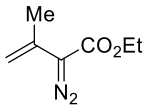
**2.3 Preparation of vinyldiazo compounds 1m-1u.**[4]




***Synthesis of S5:*** To a solution of ethyl diazoacetate (12 mmol, 1.2 equiv.) and ketone (10 mmol, 1.0 equiv.) in anhydrous THF (10.0 mL) was added LDA (12.5 mmol, 1.0 M in THF) over 20 min at -78 °C. After stirring at -78 °C for 2.5 h, the reaction was quenched by the addition of saturated $NH_4Cl$ (15 mL). The solution was extracted with $Et_2O$ (3 × 25 mL), and the combined organic layers were washed with brine (25 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed in *vacuo* and the crude product was purified by column chromatography using ethyl acetate/hexanes (20:80, v/v) as the eluent to give the *β*-hydroxy-*α*-diazo ester **S5** as yellow oil.

***Synthesis of 1m-1u:*** To a solution of **S5** and $Et_3N$ (4.0 equiv.) in $CH_2Cl_2$ (0.33 M) at 0 °C was slowly added a solution of $POCl_3$ (1.5 equiv.) in $CH_2Cl_2$ over 20 minutes. The resulting solution was warmed to room temperature and stirred for 2 h. The solution was washed with water and dried over anhydrous $Na_2SO_4$. The crude product was purified by flash chromatography to afford desired β-substituted vinyldiazoacetates **1m-1u** as red oil.

**ethyl 2-diazo-3-methylbut-3-enoate (1m)**



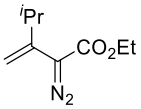

Red oil. (0.826 g, 45% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.51 – 5.20 (m, 1H), 5.06 – 4.83 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.99 – 1.86 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.2, 127.1, 110.0, 60.7, 21.3, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_7H_{11}N_2O_2$ 155.0815; Found 155.0813.

**ethyl 2-diazo-4-methyl-3-methylenepentanoate (1n)**



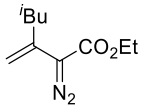

Red oil. (1.123 g, 62% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.44 (s, 1H), 5.02 (d, *J* = 1.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.52 – 2.42 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 3H), 1.12 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.7, 138.4, 107.8, 60.7, 30.7, 21.8, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{15}N_2O_2$ 183.1128; Found 183.1124.

**ethyl 2-diazo-5-methyl-3-methylenehexanoate (1o)**



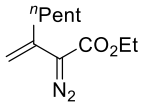

Red oil. (1.498 g, 76% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.43 (s, 1H), 4.90 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.11 (d, *J* = 7.1 Hz, 2H), 1.75 – 1.61 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.94 (s, 3H), 0.93 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.4, 130.7, 111.3, 60.7, 44.1, 27.1, 22.2, 14.4.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{17}N_2O_2$ 197.1285; Found 197.1279.

**ethyl 2-diazo-3-methyleneoctanoate (1p)**



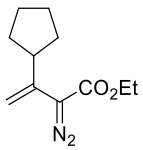

Red oil. (0.962 g, 69% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.38 (s, 1H), 4.92 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.20 (t, 2H), 1.50 – 1.39 (m, 2H), 1.34 – 1.27 (m, 7H), 0.89 (t, *J* = 6.8 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.5, 131.9, 109.9, 60.8, 34.6, 31.3, 28.3, 22.5, 14.5, 14.1.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{19}N_2O_2$ 211.1441; Found 211.1440.

**ethyl 3-cyclopentyl-2-diazobut-3-enoate (1q)**



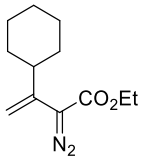

Red oil. (1.387 g, 67% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.46 (s, 1H), 5.00 (d, *J* = 1.4 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.55 (p, *J* = 8.0 Hz, 1H), 1.91 – 1.79 (m, 2H), 1.76 – 1.67 (m, 2H), 1.67 – 1.55 (m, 2H), 1.55 – 1.44 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.7, 135.6, 107.6, 60.8, 42.9, 31.6, 24.8, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}N_2O_2$ 209.1285; Found 209.1282.

**ethyl 3-cyclohexyl-2-diazobut-3-enoate (1r)**



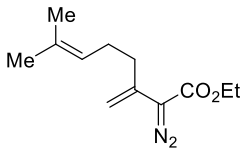

Red oil. (1.693 g, 76% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.38 (s, 1H), 4.97 (s, 1H), 4.24 (d, *J* = 7.1 Hz, 2H), 2.11 – 1.99 (m, 1H), 1.88 – 1.74 (m, 4H), 1.75 – 1.65 (m, 1H), 1.34 – 1.14 (m, 8H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.7, 137.6, 108.3, 60.7, 40.8, 32.6, 26.7, 26.3, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}N_2O_2$ 223.1441; Found 223.1436.

**ethyl 2-diazo-7-methyl-3-methyleneoct-6-enoate (1s)**



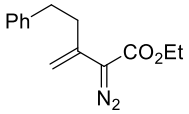

Red oil. (1.643 g, 74% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.37 (s, 1H), 5.15 – 5.07 (m, 1H), 4.94 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.27 – 2.19 (m, 2H), 2.18 – 2.09 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.4, 132.5, 131.7, 123.0, 110.1, 60.8, 34.5, 27.3, 25.7, 17.7, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}N_2O_2$ 223.1441; Found 223.1438.

**ethyl 2-diazo-3-methylene-5-phenylpentanoate (1t)**



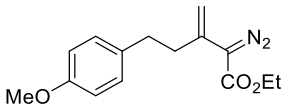

Red oil. (1.606 g, 66% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.31 – 7.26 (m, 2H), 7.23 – 7.12 (m, 3H), 5.31 (s, 1H), 4.95 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.82 – 2.73 (m, 2H), 2.59 – 2.49 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.2, 141.2, 131.7, 128.5, 126.1, 110.3, 60.9, 36.5, 35.4, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2$ 245.1285; Found 245.1281.

**ethyl 2-diazo-5-(4-methoxyphenyl)-3-methylenepentanoate (1u)**




Red oil. (1.930 g, 70% yield over two steps, eluent: petroleum ether/ethyl acetate = 100/1, v/v).

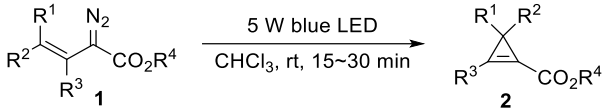
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.18 – 7.07 (m, 2H), 6.91 – 6.77 (m, 2H), 5.34 (s, 1H), 4.96 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.88 – 2.69 (m, 2H), 2.61 – 2.43 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** ) δ 165.2, 158.0, 133.2, 131.7, 129.3, 113.8, 110.3, 60.8, 55.3, 36.8, 34.5, 14.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2$ 275.1390; Found 275.1383.

## 3. Experimental procedure for the denitrogenative cyclization

### 3.1 General experimental procedure for the cyclization of vinyl diazoacetates 1




A dry reaction tube equipped with a magnetic stirring bar was charged with vinyldiazo compound **1** (0.10 mmol), $CHCl_3$ 0.5 mL under ambient atmosphere. The tube was irradiated with a 5 W blue LED at room temperature with fan cooling (about 25 °C) for 15-30 min. The reaction can be monitored according to the color fading, usually from orange to colorless or light yellow. Upon completion, the solvent was removed under reduced pressure (< 30°C).

The reactions of β-substituted vinyldiazoacetates **1p**, **1q**, **1s** and **1u** contains minor amounts of pyrazoles as the by-products, which can be removed by the rapid silica gel (3–5 cm) filtration using dichloromethane as the eluent. For other reactions, the yields were quotative and the resulting cyclopropenes were characterized directly without further purification.

### 3.2 Experimental procedure for the synthesis of cyclopropene on gram scale

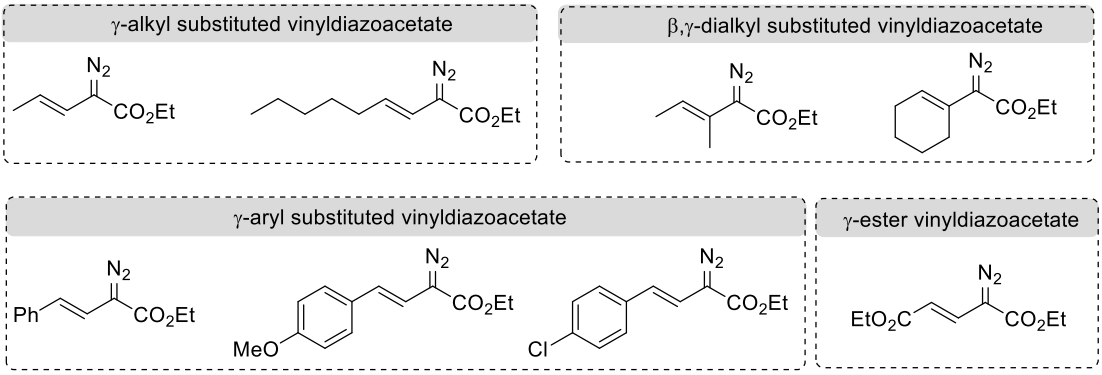
A dry reaction tube equipped with a magnetic stirring bar was charged with **1a** (2.3 g, 10 mmol) and $CHCl_3$ (50 mL) under ambient atmosphere, seal the tube and use a balloon to balance the pressure. The mixture was irradiated with a 5 W blue LED with fan cooling at room temperature for 2-4 h. The reaction progress was monitored by the fading of the characteristic diazo coloration. Upon completion, the solvent was removed under reduced pressure (<30 °C, to reduce the loss of volatile products), and the crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 40:1, v/v) to afford **2a** as a pale-yellow oil (86% yield, 1.74 g).

The gram synthesis of cyclopropenes **2b**, **2k** and **2m** used the same experimental procedure as described above.

### 3.3 Unsuccessful examples

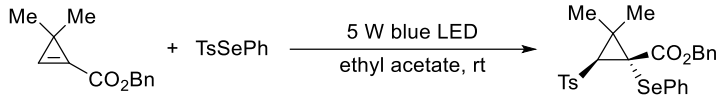
The current method is limited to the conversion of γ,γ-dialkyl vinyldiazoacetates and β-alkyl vinyldiazoacetates to the corresponding cyclopropene-1-carboxylates. Vinyldiazoacetates bearing γ-aryl, β,γ-dialkyl and γ-ester group were unsuccessful. These substrates led to complex mixtures and it's hard for us to isolate and identify the resultant side-products. The results on the basis of GC-MS analysis were briefly discussed below.

γ-Aryl vinyldiazoacetates do not generate cyclopropenes but provide pyrazole and carbene dimerization as the major side products. For β,γ-dialkyl vinyldiazoacetates, the situation is more complicated. Except for the above-mentioned side-products, they might form unstable cyclopropenes, which further undergo Alder-Ene reaction, 1,3-dipolar addition with another molecule of β,γ-dialkyl vinyldiazoacetates, reversible ring-opening et al. We also examined the vinyldiazoacetate bearing an ester group on the γ-position, no cyclopropene was formed either.



## 4. Experimental procedure for transformations of 2a

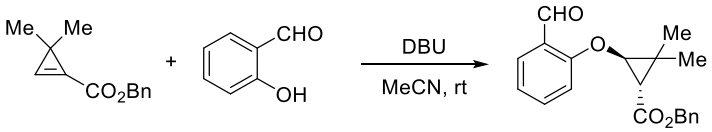
### 4.1 Radical 1,2-addition of TsSePh to 2a




**2a** **3**, 70%

Into an oven-dried reaction vial flushed with $N_2$, **2a** (0.20 mmol, 1.0 equiv.) and selenosulfonates (0.20 mmol, 1.0 equiv.) in EtOAc (1.0 mL) was stirred at room temperature under the irradiation of a 5 W blue LED for 2 h. After the removal of solvent in vacuo, the residue was purified by column chromatography (petroleum ether /ethyl acetate = 5:1) to afford product **3** in 70% yield (72.2 mg) as a pale-yellow solid.

### 4.2 Michael addition of salicylaldehyde to 2a




**2a** **4**, 72%

The solution of **2a** (0.20 mmol, 1.0 equiv.), salicylaldehyde (0.20 mmol, 1.0 equiv.) and DBU (0.03 mmol, 15 mol%) in MeCN (2.0 mL) was stirred at room temperature under ambient atmosphere for 24 h. Filter to remove insoluble substances then remove solvent in vacuo, the residue was purified by column chromatography (petroleum ether /ethyl acetate = 5:1) to afford product **4** in 72% yield (46.8 mg) as a pale-yellow oil.

## 5. Decay plots from the kinetic experiments

### 5.1 General procedure for the kinetic measurements

Compounds **2a** and **2m** were synthesized according to the procedure described above. For kinetic analysis, each compound was dissolved in deuterated solvent (0.5 mL) at a defined concentration. 1,3,5-trimethoxybenzene was added as an internal standard. The time-dependent ratio of remain-to-initial concentration ($1/C_t$-$1/C_0$) was monitored by $^1$H NMR spectroscopy at predetermined intervals (400 MHz). NMR integration values were normalized against the internal standard to quantify reaction progress.

For compound **2a**, the olefinic proton resonance (δ =7.98) served as the characteristic resonance for quantification. In the case of compound 2b, the allylic methyl protons (δ = 2.34) were selected as the characteristic resonance.

Half-life was calculated from straight lines obtained by ($1/C_t$-$1/C_0$) or $\ln(C_t/C_0)$ plots.

### 5.2 Decay of compound 2a

**Table S1.** The decay of **2a ($C_0$ =** 0.1M**)** in $CDCl_3$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.100 | 0.100 | 0.100 | 0.000 | 0.000 |
| 12 | 0.090 | 0.090 | 0.090 | 0.000 | 1.127 |
| 24 | 0.083 | 0.086 | 0.084 | 0.002 | 1.848 |
| 36 | 0.078 | 0.080 | 0.079 | 0.001 | 2.635 |
| 48 | 0.075 | 0.075 | 0.075 | 0.000 | 3.374 |

**Table S2.** The decay of **2a ($C_0$ =** 0.3M**)** in $CDCl_3$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.300 | 0.000 | 0.000 |
| 12 | 0.266 | 0.260 | 0.263 | 0.005 | 0.466 |
| 24 | 0.250 | 0.245 | 0.248 | 0.003 | 0.702 |
| 36 | 0.229 | 0.223 | 0.226 | 0.004 | 1.094 |
| 48 | 0.207 | 0.198 | 0.203 | 0.006 | 1.599 |

**Table S3.** The decay of **2a** ($C_0$=0.5M) in $CDCl_3$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.500 | 0.500 | 0.500 | 0.000 | 0.000 |
| 12 | 0.425 | 0.428 | 0.426 | 0.002 | 0.345 |
| 24 | 0.361 | 0.363 | 0.362 | 0.001 | 0.763 |
| 36 | 0.310 | 0.324 | 0.317 | 0.010 | 1.156 |
| 48 | 0.276 | 0.265 | 0.271 | 0.008 | 1.694 |

**Table S4.** Rate constants and half-lives for **2a** in $CDCl_3$ at 25 °C at different concentrations.

| Entry | Concentration (mol/L) | $k_{obs}(h^{-1})$ | Half-life |
|---|---|---|---|
| 1 | 0.1 | 0.0627 | 159h 29min |
| 2 | 0.3 | 0.0316 | 105h 29min |
| 3 | 0.5 | 0.0370 | 54h 3min |

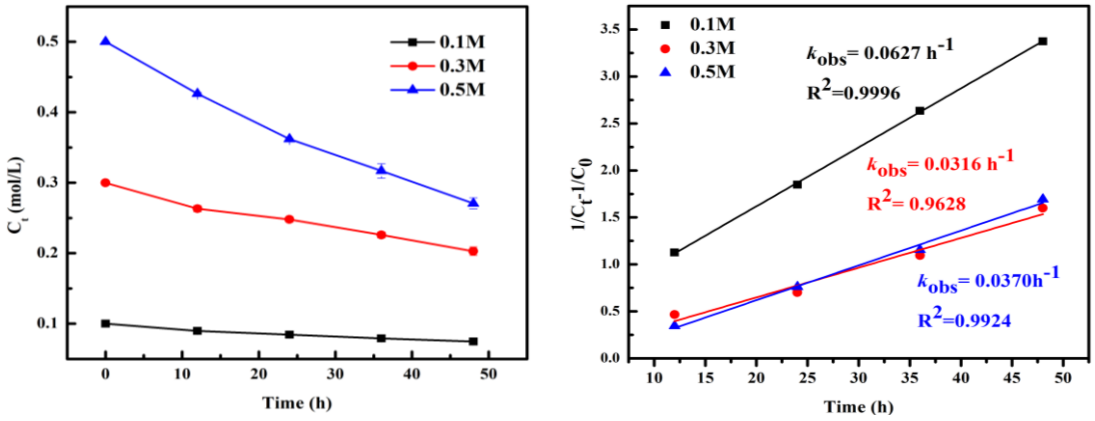



**Figure S1**. The $C_t$ of **2a** in $CDCl_3$ at 25 °C over time at different concentration (left) and the linear plot of ($1/C_t$-$1/C_0$) vs time (right).

**Table S5.** The decay of **2a** ($C_0$ = 0.3M) in $CD_3OD$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ | $C_t/C_0$ 1 | $C_t/C_0$ 2 | $C_t/C_0$ mean | Error | $\ln(C_t/C_0)$ mean |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.300 | 0.000 | 0.000 | 1.000 | 1.000 | 1.000 | 0.000 | 0.000 |
| 12 | 0.151 | 0.145 | 0.148 | 0.004 | 3.406 | 0.505 | 0.485 | 0.495 | 0.014 | -0.704 |
| 24 | 0.089 | 0.084 | 0.087 | 0.003 | 8.217 | 0.296 | 0.281 | 0.289 | 0.010 | -1.243 |
| 36 | 0.052 | 0.053 | 0.053 | 0.000 | 15.671 | 0.175 | 0.176 | 0.175 | 0.001 | -1.741 |
| 48 | 0.034 | 0.035 | 0.034 | 0.001 | 25.678 | 0.112 | 0.118 | 0.115 | 0.004 | -2.164 |

**Table S6.** The decay of **2a** ($C_0$ = 0.3M) in DMSO at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t-1/C_0$ | $C_t/C_0$ 1 | $C_t/C_0$ 2 | $C_t/C_0$ mean | Error | $\ln(C_t/C_0)$ mean |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.300 | 0.000 | 0.000 | 1.000 | 1.000 | 1.000 | 0.000 | 0.000 |
| 12 | 0.138 | 0.137 | 0.137 | 0.001 | 3.944 | 0.459 | 0.457 | 0.458 | 0.002 | -0.781 |
| 24 | 0.059 | 0.060 | 0.059 | 0.001 | 13.521 | 0.196 | 0.200 | 0.198 | 0.003 | -1.621 |
| 36 | 0.028 | 0.029 | 0.028 | 0.001 | 31.792 | 0.093 | 0.097 | 0.095 | 0.003 | -2.355 |
| 48 | 0.015 | 0.015 | 0.015 | 0.000 | 62.637 | 0.050 | 0.051 | 0.051 | 0.001 | -2.985 |

**Table S7.** Rate constants and half-lives for **2a** ($C_0$ = 0.3M) in $CD_3OD$ and DMSO at 25 °C

| Entry | Solvent | Model | $k_{obs}(h^{-1})$ | Half-life |
|---|---|---|---|---|
| 1 | $CD_3OD$ | second-order kinetics | 0.6189 | 5h 23min |
| 2 | DMSO | second-order kinetics | 1.6196 | 2h 3min |
| 3 | $CD_3OD$ | first-order kinetics | 0.0447 | 13h 19min |
| 4 | DMSO | first-order kinetics | 0.0629 | 10h 23min |

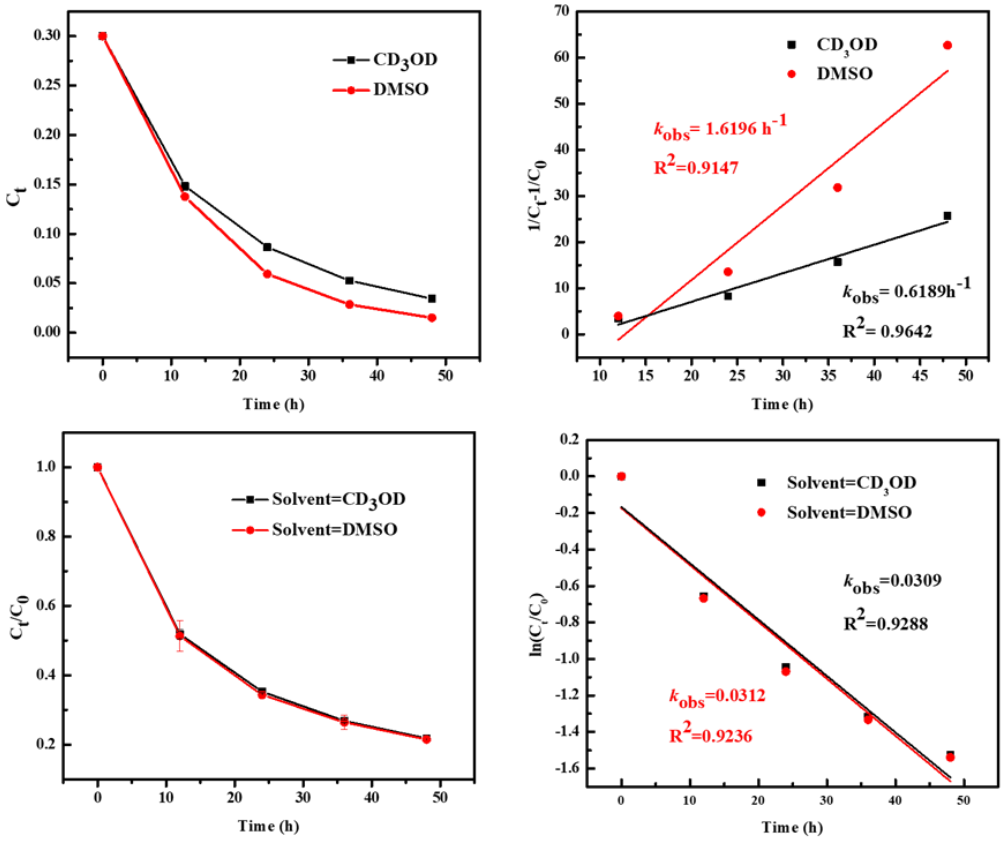



**Figure S2.** The $C_t$ of **2a** ($C_0$ = 0.3M) in DMSO and $CD_3OD$ at 25 °C over time (top-left) and the linear plot of ($1/C_t-1/C_0$) vs time (top-right).The $C_t/C_0$ of **2a** (0.3M) in DMSO and $CD_3OD$ at 25 °C over time (lower-left) and the linear plot of $\ln(C_t/C_0)$ vs time (lower-right).

**Table S8.** The decay of **2a** ($C_0$ = 0.3M) in $CDCl_3$ at 50 °C over time.

| Time (min) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.000 | 0.300 | 0.000 |
| 3 | 0.294 | 0.293 | 0.001 | 0.294 | 0.071 |
| 8 | 0.284 | 0.289 | 0.004 | 0.286 | 0.157 |
| 18 | 0.280 | 0.279 | 0.001 | 0.280 | 0.243 |
| 30 | 0.275 | 0.266 | 0.006 | 0.270 | 0.367 |
| 50 | 0.248 | 0.237 | 0.008 | 0.242 | 0.791 |
| 70 | 0.237 | 0.233 | 0.003 | 0.235 | 0.916 |
| 90 | 0.221 | 0.225 | 0.003 | 0.223 | 1.157 |
| 120 | 0.212 | 0.206 | 0.005 | 0.209 | 1.458 |
| 150 | 0.179 | 0.172 | 0.005 | 0.175 | 2.373 |
| 180 | 0.163 | 0.163 | 0.001 | 0.163 | 2.802 |
| 210 | 0.161 | 0.152 | 0.007 | 0.157 | 3.056 |
| 240 | 0.156 | 0.130 | 0.018 | 0.143 | 3.666 |
| 270 | 0.139 | 0.115 | 0.017 | 0.127 | 4.557 |

**Table S9.** Rate constants and half-lives for **2a** ($C_0$ = 0.3M) in $CDCl_3$ at 50 °C.

| Entry | Temperature (°C) | $k_{obs}$($min^{-1}$) | Half-life |
|---|---|---|---|
| 1 | T=50 °C | 0.0160 | 3h 28min |

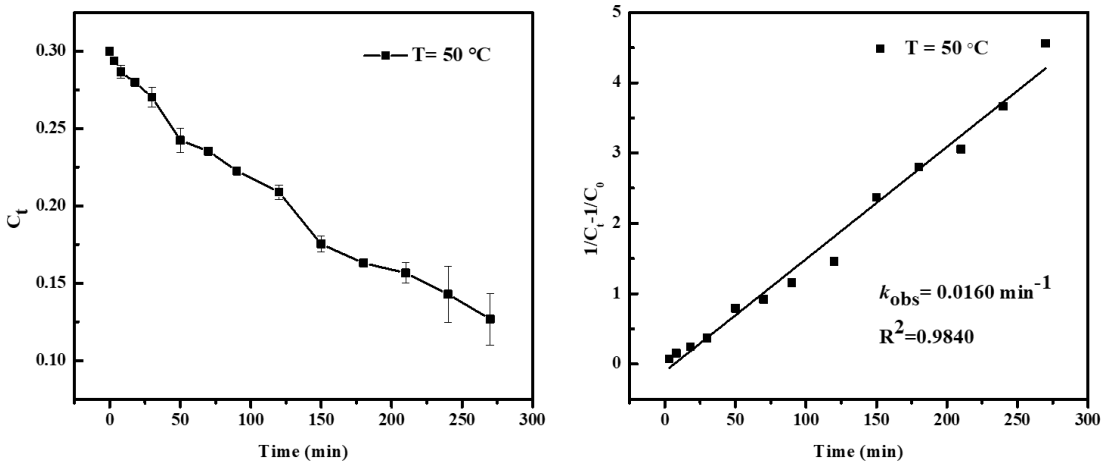



**Figure S3**. The decay of **2a** ($C_0$ = 0.3M) in $CDCl_3$ at 50 °C over time (left) and the linear plot of ($1/C_t$-$1/C_0$) vs time (right).

### 5.3 Decay of compound 2m

**Table S10.** The decay of **2m** ($\mathbf{C_0}$ = 0.1M) in $CDCl_3$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.100 | 0.100 | 0.100 | 0.000 | 0.000 |
| 12 | 0.088 | 0.089 | 0.089 | 0.000 | 1.285 |
| 24 | 0.079 | 0.081 | 0.080 | 0.001 | 2.510 |
| 36 | 0.072 | 0.076 | 0.074 | 0.003 | 3.584 |
| 48 | 0.064 | 0.069 | 0.066 | 0.003 | 5.042 |

**Table S11.** The decay of **2m** ($\mathbf{C_0}$ = 0.3M) in $CDCl_3$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.300 | 0.000 | 0.000 |
| 12 | 0.210 | 0.211 | 0.211 | 0.001 | 1.416 |
| 24 | 0.178 | 0.172 | 0.175 | 0.004 | 2.381 |
| 36 | 0.150 | 0.145 | 0.148 | 0.004 | 3.434 |
| 48 | 0.127 | 0.124 | 0.125 | 0.002 | 4.637 |

**Table S12.** The decay of **2m** ($\mathbf{C_0}$ = 0.5M) in $CDCl_3$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.500 | 0.500 | 0.500 | 0.000 | 0.000 |
| 12 | 0.331 | 0.337 | 0.334 | 0.004 | 0.992 |
| 24 | 0.257 | 0.263 | 0.260 | 0.005 | 1.843 |
| 36 | 0.207 | 0.210 | 0.209 | 0.002 | 2.796 |
| 48 | 0.175 | 0.181 | 0.178 | 0.004 | 3.618 |

**Table S13.** Rate constants and half-lives for **2m** in $CDCl_3$ at 25 °C at different concentrations.

| Entry | Concentration (mmol/mL) | $K_{obs}(h^{-1})$ | Half-life |
|---|---|---|---|
| 1 | 0.1 | 0.1029 | 97h 11min |
| 2 | 0.3 | 0.0893 | 37h 20min |
| 3 | 0.5 | 0.0736 | 27h 10min |

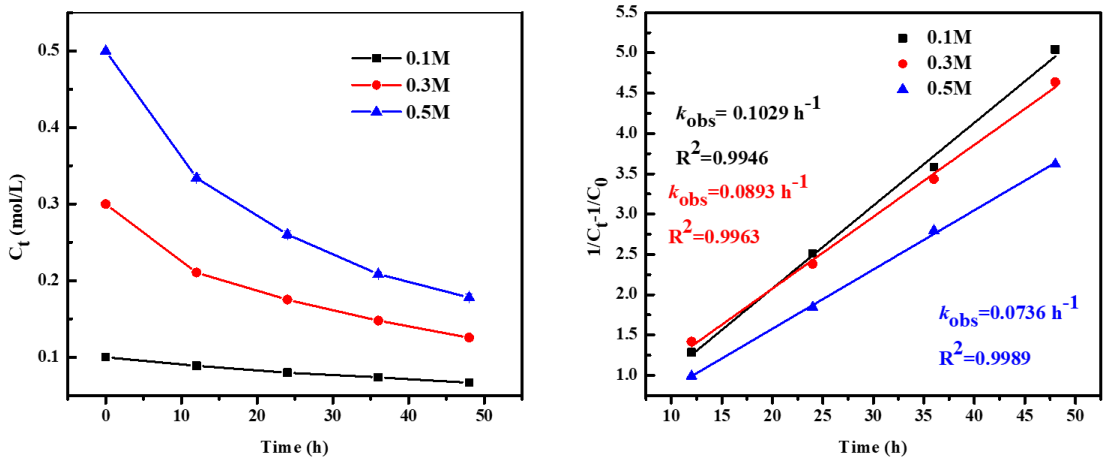



**Figure S4**. The $C_t$ of **2m** in $CDCl_3$ at 25 °C over time at different concentration (left) and the linear plot of $(1/C_t\text{-}1/C_0)$ vs time (right).

**Table S14.** The decay of **2m** ($\mathbf{C_0}$ = 0.3M) in $CD_3OD$ at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t\text{-}1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.300 | 0.000 | 0.000 |
| 12 | 0.158 | 0.153 | 0.155 | 0.004 | 0.258 |
| 24 | 0.105 | 0.106 | 0.106 | 0.001 | 0.255 |
| 36 | 0.080 | 0.081 | 0.080 | 0.001 | 0.253 |
| 48 | 0.065 | 0.065 | 0.065 | 0.000 | 0.249 |

**Table S15.** The decay of **2m** ($\mathbf{C_0}$ = 0.3M) in DMSO at 25 °C over time.

| Time (h) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t\text{-}1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.300 | 0.000 | 0.000 |
| 12 | 0.163 | 0.144 | 0.154 | 0.013 | 0.264 |
| 24 | 0.105 | 0.101 | 0.103 | 0.003 | 0.266 |
| 36 | 0.084 | 0.075 | 0.079 | 0.006 | 0.258 |
| 48 | 0.065 | 0.064 | 0.064 | 0.001 | 0.254 |

**Table S16.** Rate constants and half-lives for **2m** ($\mathbf{C_0}$ = 0.3M) in $CDCl_3$ at 25 °C in $CD_3OD$ and DMSO.

| Entry | Solvent | $K_{obs}(h^{-1})$ | Half-life |
|---|---|---|---|
| 1 | $CD_3OD$ | 0.2468 | 13h 30min |
| 2 | DMSO | 0.2503 | 13h 19min |

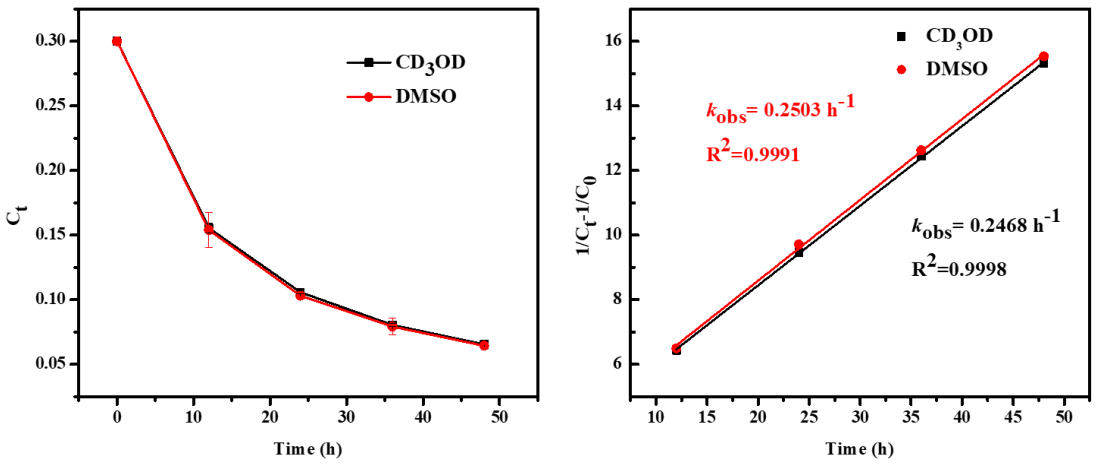



**Figure S5.** The decay of **2m** ($C_0$ = 0.3M) in DMSO and $CD_3OD$ at 25 °C over time (left) and the linear plot of ($1/C_t$-$1/C_0$) vs time (right).

**Table S17.** The decay of **2a** ($C_0$ = 0.3M) in $CDCl_3$ at 50 °C over time.

| Time (min) | $C_t$ 1 | $C_t$ 2 | $C_t$ mean | Error | $1/C_t$-$1/C_0$ |
|---|---|---|---|---|---|
| 0 | 0.300 | 0.300 | 0.300 | 0.000 | 0.000 |
| 30 | 0.264 | 0.265 | 0.265 | 0.000 | 0.015 |
| 60 | 0.237 | 0.229 | 0.233 | 0.005 | 0.016 |
| 90 | 0.216 | 0.205 | 0.210 | 0.008 | 0.016 |
| 120 | 0.191 | 0.190 | 0.191 | 0.001 | 0.016 |
| 150 | 0.176 | 0.173 | 0.174 | 0.002 | 0.016 |
| 180 | 0.163 | 0.159 | 0.161 | 0.003 | 0.016 |
| 210 | 0.148 | 0.147 | 0.148 | 0.000 | 0.016 |
| 240 | 0.143 | 0.141 | 0.142 | 0.001 | 0.016 |
| 270 | 0.137 | 0.131 | 0.134 | 0.005 | 0.015 |

**Table S18.** Rate constants and half-lives for **2a** (0.3M) in $CDCl_3$ at 50 °C .

| Entry | Temperature (°C) | $K_{obs}$($min^{-1}$) | Half-life |
|---|---|---|---|
| 1 | T=50 °C | 0.0156 | 3h 34min |

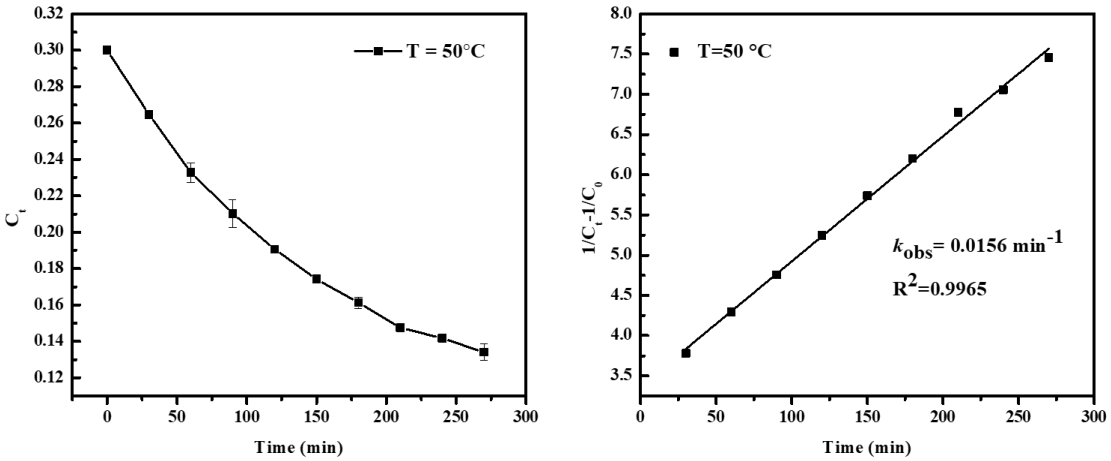
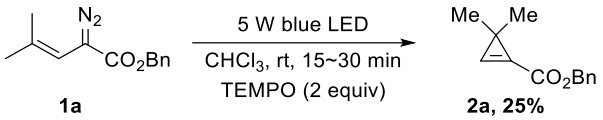



**Figure S6**. The decay of **2m** (0.3M) in $CDCl_3$ at 50 °C over time (left) and the linear plot of $(1/C_t - 1/C_0)$ vs time (right).

## 6. Mechanism studies

### 6.1 Radical inhibition experiment




**1a** **2a, 25%**

A dry reaction tube equipped with a magnetic stirring bar was charged with vinyldiazo compound **1a** (0.10 mmol, 23 mg), TEMPO (0.20 mmol, 31.3 mg), $CHCl_3$ 0.5 mL under ambient atmosphere, obtain a clear red liquid. The tube was irradiated with a 5 W blue LED at room temperature with fan cooling (about 25 °C) for about 15 min. The reaction was monitored by TLC, due to the red color of TEMPO. After complete conversion of substance **1a**, the resulting organic solution was supplemented with 1,3,5-trimethoxybenzene as an internal standard, resulting in a 25% yield of **2a** as determined by $^1$H-NMR spectroscopy.

### 6.2 UV−Vis absorption spectra of 1a and emission wavelength of LEDs

The UV−Vis spectra were recorded in $CHCl_3$, using 0.10 M concentration solutions, in a 1 cm Hellma Quartz cuvette with a cap provided with a Teflon septum.

Vinyldiazo compound **1a** present a wide absorbance spectrum in the visible region.

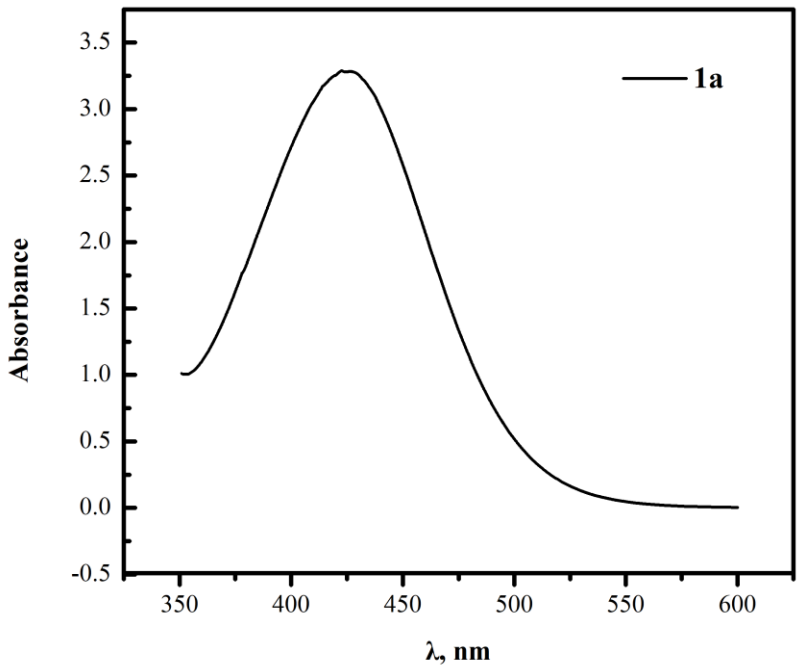



**Figure S7**. UV−Vis absorption spectrm of **1a**

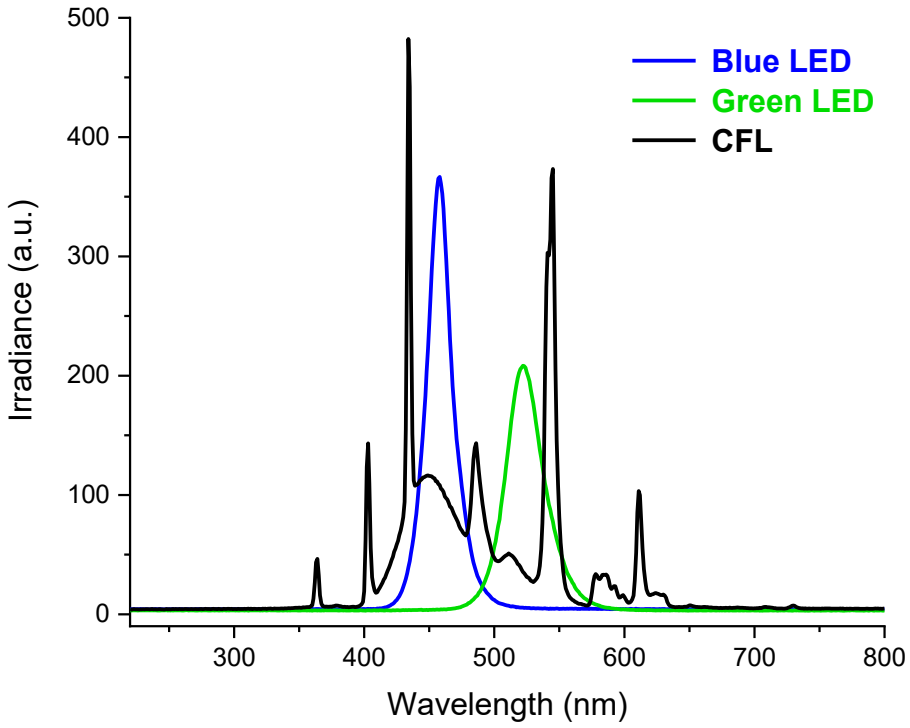
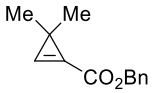



**Figure S8**. Emission wavelength of LEDs

## 7. Characterization data

**benzyl 3,3-dimethylcycloprop-1-ene-1-carboxylate (2a)**



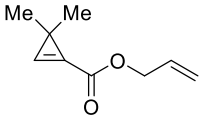

Pale-yellow oil; Yield: >99% (20.2 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.98 (s, 1H), 7.41 – 7.33 (m, 5H), 5.26 (s, 2H), 1.30 (s, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.6, 135.7, 134.3, 128.6, 128.4, 128.3, 127.8, 66.7, 26.9, 24.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}O_2$ 203.1067; Found 203.1063.

**allyl 3,3-dimethylcycloprop-1-ene-1-carboxylate (2b)**



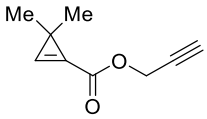

Pale-yellow oil; Yield: >99% (15.2 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.98 (s, 1H), 6.09 – 5.89 (m, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.71 (d, *J* = 5.5 Hz, 2H), 1.29 (s, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.4, 134.1, 131.9, 127.8, 118.6, 65.6, 26.9, 24.4.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{13}O_2$ 153.0910; Found 153.0910.

**prop-2-yn-1-yl 3,3-dimethylcycloprop-1-ene-1-carboxylate (2c)**



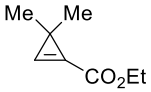

Pale-yellow oil; Yield: >99% (15.0 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.05 (s, 1H), 4.81 (d, *J* = 2.5 Hz, 2H), 2.51 (t, *J* = 2.5 Hz, 1H), 1.30 (s, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 160.7, 135.5, 127.2, 77.2, 75.3, 52.4, 26.8, 24.7.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{11}O_2$ 151.0754; Found 151.0752.

**ethyl 3,3-dimethylcycloprop-1-ene-1-carboxylate (2d)**



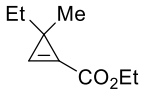

Pale-yellow oil; Yield: >99% (14.0 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.96 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.8, 133.2, 128.0, 61.0, 26.8, 24.2, 14.2.

**HRMS** (ESI) calcd for $C_8H_{13}O_2$ $[M+H]^+$: 141.0910; found: 141.0915.

**ethyl 3-ethyl-3-methylcycloprop-1-ene-1-carboxylate (2e)**



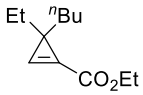

Pale-yellow oil; Yield: >99% (15.4 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.92 (s, 1H), 4.27 (qd, *J* = 7.1, 2.2 Hz, 2H), 1.70 – 1.53 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 3H), 0.74 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 162.0, 131.9, 126.5, 61.0, 31.4, 29.7, 25.2, 14.2, 11.4.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{15}O_2$ 155.1067; Found 155.1064.

**ethyl 3-butyl-3-ethylcycloprop-1-ene-1-carboxylate (2f)**



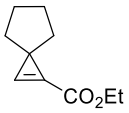

Pale-yellow oil; Yield: >99% (19.6 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.88 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.74 – 1.44 (m, 4H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.25 (q, 2H), 1.17 – 0.96 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H), 0.70 (t, *J* = 7.6 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 162.1, 130.3, 124.7, 61.0, 36.9, 34.4, 29.8, 29.4, 22.7, 14.2, 14.1, 11.4.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{21}O_2$ 197.1536; Found 197.1537.

**ethyl spiro[2.4]hept-1-ene-1-carboxylate (2g)**



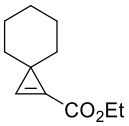

Pale-yellow oil; Yield: >99% (16.6 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.83 – 1.63 (m, 6H), 1.55 – 1.43 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.5, 128.5, 122.9, 61.0, 35.8, 33.9, 26.4, 14.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}O_2$ 167.1067; Found 167.1061.

**ethyl spiro[2.5]oct-1-ene-1-carboxylate (2h)**



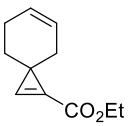

Pale-yellow oil; Yield: >99% (18.0 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.02 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.69 – 1.42 (m, 10H), 1.33 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 160.8, 132.6, 127.7, 60.0, 37.2, 30.8, 25.5, 25.4, 13.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}O_2$ 181.1223; Found 181.1217.

**ethyl spiro[2.5]octa-1,5-diene-1-carboxylate (2i)**



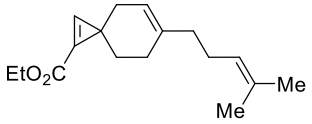

Pale-yellow oil; Yield: >99% (17.8 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.92 (s, 1H), 5.80 – 5.67 (m, 1H), 5.66 – 5.53 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.26 – 2.03 (m, 3H), 2.02 – 1.89 (m, 1H), 1.73 – 1.61 (m, 3H), 1.60 – 1.47 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 161.6, 131.7, 127.4, 127.2, 127.0, 61.1, 37.2, 33.9, 28.7, 25.5, 14.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}O_2$ 179.1067; Found 179.1067.

**ethyl 6-(4-methylpent-3-en-1-yl)spiro[2.5]octa-1,5-diene-1-carboxylate (2j)**



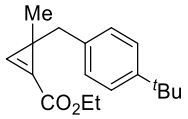

Pale-yellow oil; Yield: >99% (26.0 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1). Mixture of E- and Z- isomers (E/Z = 2:1)

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.00 (s, 1H), 5.56 – 5.31 (m, 1H), 5.17 – 5.02 (m, 1H), 4.32 – 4.19 (m, 2H), 2.26 – 1.88 (m, 8H), 1.77 – 1.69 (m, 1H), 1.72 – 1.65 (m, 3H), 1.63 – 1.56 (m, 3H), 1.58 – 1.46 (m, 1H), 1.36 – 1.28 (m, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.65, 161.61, 138.2, 137.8, 132.0, 131.9, 131.4, 127.22, 127.17, 124.4, 124.3, 121.0, 120.5, 61.1, 40.2, 38.0, 37.6, 37.0, 34.1, 33.7, 29.1, 28.8, 28.7, 26.6, 26.5, 25.74, 25.71, 25.2, 17.7, 14.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}O_2$ 261.1849; Found 261.1847.

**ethyl 3-(4-(tert-butyl)benzyl)-3-methylcycloprop-1-ene-1-carboxylate (2k)**



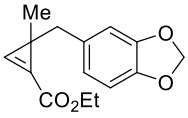

Pale-yellow oil; Yield: >99% (27.2 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.88 (s, 1H), 7.34 – 7.26 (m, 2H), 7.13 – 7.04 (m, 2H), 4.37 – 4.21 (m, 2H), 2.97 – 2.85 (m, 2H), 1.36 (d, *J* = 7.1 Hz, 3H), 1.34 – 1.33 (m, 3H), 1.33 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.5, 148.7, 136.6, 131.5, 129.0, 126.3, 125.1, 61.1, 45.6, 34.4, 31.4, 29.4, 25.2, 14.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}O_2$ 273.1849; Found 273.1844.

**ethyl 3-(benzo[d][1,3]dioxol-5-ylmethyl)-3-methylcycloprop-1-ene-1-carboxylate (2l)**



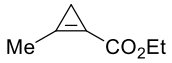

Pale-yellow oil; Yield: >99% (26.0 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.81 (s, 1H), 6.73 – 6.66 (m, 1H), 6.65 – 6.59 (m, 1H), 6.56 – 6.50 (m, 1H), 5.91 (s, 2H), 4.36 – 4.16 (m, 2H), 2.84 (d, *J* = 3.5 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.4, 147.5, 145.7, 133.5, 131.1, 125.8, 122.2, 109.7, 108.0, 100.7, 61.1, 45.5, 29.6, 25.2, 14.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}O_4$ 261.1121; Found 261.1120.

**ethyl 2-methylcycloprop-1-ene-1-carboxylate (2m)**



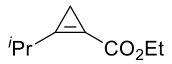

Pale-yellow oil; Yield: >99%, determined by $^1$H NMR; $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 4.29 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.39 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.7, 131.0, 103.7, 60.9, 14.3, 13.2, 11.0.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_7H_{11}O_2$ 127.0754; Found 127.0755.

**ethyl 2-isopropylcycloprop-1-ene-1-carboxylate (2n)**



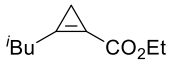

Pale-yellow oil; Yield: >99% (15.4 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 4.26 (q, *J* = 7.1 Hz, 2H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.36 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.24 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.8, 139.0, 101.6, 60.9, 27.7, 19.8, 14.3, 9.8.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_9H_{15}O_2$ 155.1067; Found 155.1062.

**ethyl 2-isobutylcycloprop-1-ene-1-carboxylate (2o)**




Pale-yellow oil; Yield: >99% (16.8 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 4.29 (q, *J* = 7.1 Hz, 2H), 2.58 (d, *J* = 6.7 Hz, 2H), 2.14 – 2.05 (m, 1H), 1.38 (s, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 165.4, 130.7, 111.3, 60.7, 44.1, 27.1, 22.2, 14.4.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{17}O_2$ 169.1223; Found 169.1221.

**ethyl 2-pentylcycloprop-1-ene-1-carboxylate (2p)**

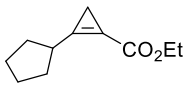

Pale-yellow oil; Yield: 92% (10.2 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 4.26 (q, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 1.75 – 1.62 (m, 2H), 1.52 – 1.18 (m, 9H), 0.99 – 0.73 (m, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.8, 134.8, 102.8, 60.9, 31.4, 27.7, 26.4, 22.4, 14.3, 14.0, 10.4.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{19}O_2$ 183.1380; Found 183.1378.

**ethyl 2-cyclopentylcycloprop-1-ene-1-carboxylate (2q)**



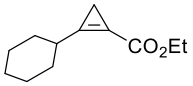

Pale-yellow oil; Yield: 93% (16.7 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 4.26 (q, *J* = 7.1 Hz, 2H), 3.21 – 3.10 (m, 1H), 2.03 – 1.86 (m, 2H), 1.78 – 1.62 (m, 6H), 1.35 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.8, 138.2, 101.2, 60.9, 37.5, 30.6, 25.5, 14.3, 9.9.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}O_2$ 181.1223; Found 181.1220.

**ethyl 2-cyclohexylcycloprop-1-ene-1-carboxylate (2r)**



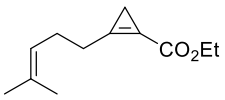

Pale-yellow oil; Yield: >99% (19.4 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 4.26 (q, *J* = 7.1 Hz, 2H), 2.78 – 2.62 (m, 1H), 2.01 – 1.84 (m, 2H), 1.75 – 1.64 (m, 2H), 1.54 – 1.41 (m, 3H), 1.40 – 1.29 (m,8H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.9, 138.0, 101.9, 60.9, 36.4, 29.9, 26.0, 25.2, 14.3, 9.5.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}O_2$ 195.1380; Found 195.1375.

**ethyl 2-(4-methylpent-3-en-1-yl)cycloprop-1-ene-1-carboxylate (2s)**



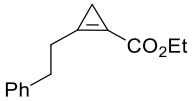

Pale-yellow oil; Yield: 93% (18.0 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 5.20 – 5.10 (m, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.37 (q, *J* = 7.4 Hz, 2H), 1.68 (s, 3H), 1.62 (s, 3H), 1.36 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.8, 134.5, 132.9, 122.9, 103.2, 60.9, 28.0, 25.7, 25.4, 17.7, 14.3, 10.6.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}O_2$ 195.1380; Found 195.1376.

**ethyl 2-phenethylcycloprop-1-ene-1-carboxylate (2t)**



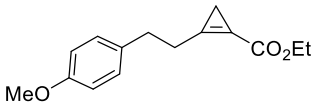

Pale-yellow oil; Yield: 90% (19.4 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.34 – 7.25 (m, 2H), 7.24 – 7.18 (m, 3H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.14 – 3.01 (m, 2H), 3.00 – 2.93 (m, 2H), 1.39 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.6, 140.8, 133.7, 128.5, 128.3, 126.3, 103.8, 61.0, 32.9, 29.5, 14.3, 10.8.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{17}O_2$ 217.1223; Found 217.1218.

**ethyl 2-(4-methoxyphenethyl)cycloprop-1-ene-1-carboxylate (2u)**



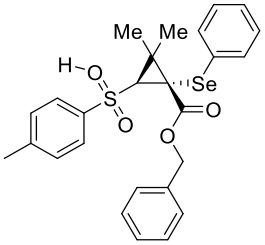

Pale-yellow oil; Yield: 92% (22.5 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 30:1).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.20 – 7.08 (m, 2H), 6.90 – 6.81 (m, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.10 – 2.91 (m, 4H), 1.40 (s, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 161.6, 158.1, 133.9, 132.9, 129.2, 113.9, 103.7, 61.0, 55.3, 32.1, 29.8, 14.3, 10.8.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}O_3$ 247.1329; Found 247.1324.

**benzyl-2,2-dimethyl-1-(phenylselanyl)-3-tosylcyclopropane-1-carboxylate (3)**



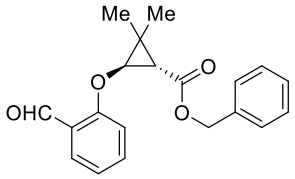

Pale-yellow solid; Yield: 70% (72.2 mg); $R_f$ = 0.4 (petroleum ether: ethyl acetate = 5:1).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** 7.82 – 7.55 (m, 2H), 7.46 – 7.36 (m, 5H), 7.35 – 7.29 (m, 2H), 7.25 – 7.17 (m, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.98 (m, 2H), 5.29 (d, *J* = 12.1 Hz, 1H), 5.17 (d, *J* = 12.1 Hz, 1H), 2.59 (s, 1H), 2.45 (s, 3H), 1.79 (s, 3H), 1.55 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 167.1, 144.1, 138.4, 135.3, 134.5, 129.6, 129.0, 129.0, 128.5, 128.4, 128.3, 127.9, 127.8, 67.8, 55.4, 39.8, 32.2, 26.7, 21.7, 18.0.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}O_4SSe$ 515.0790; Found 515.0778.

**benzyl (1SR,3RS)-3-(2-formylphenoxy)-2,2-dimethylcyclopropane-1-carboxylate (4)**




Pale-yellow oil; Yield: 72% (46.8 mg); $R_f$ = 0.3 (petroleum ether: ethyl acetate = 30:1).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 10.42 (s, 1H), 7.87 – 7.80 (m, 1H), 7.57 – 7.46 (m, 1H), 7.43 – 7.34 (m, 5H), 7.12 – 7.05 (m, 1H), 7.03 – 6.96 (m, 1H), 5.19 (q, *J* = 12.2 Hz, 2H), 4.14 (s, 1H), 1.86 (d, *J* = 2.8 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H).

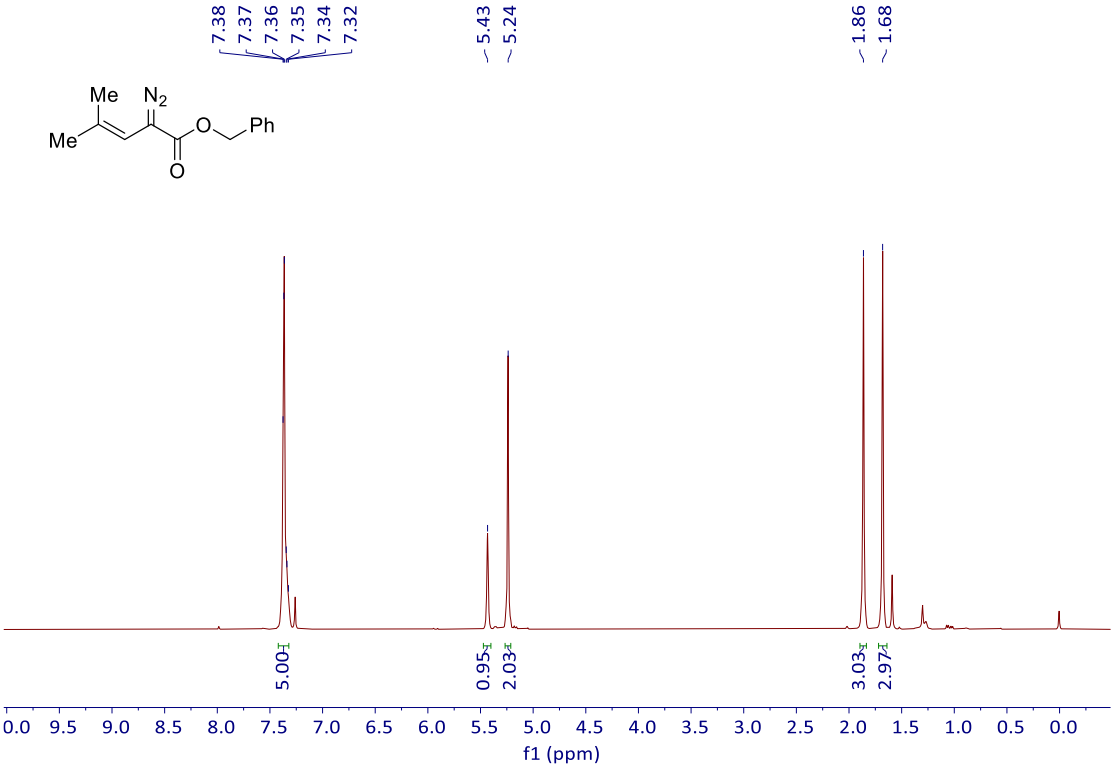
**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 189.2, 170.4, 160.6, 136.1, 128.7, 128.5, 128.4, 128.3, 124.8, 121.6, 113.3, 66.7, 66.3, 33.1, 29.9, 20.0, 18.2.

**HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}O_4$ 325.1434; Found 325.1427.

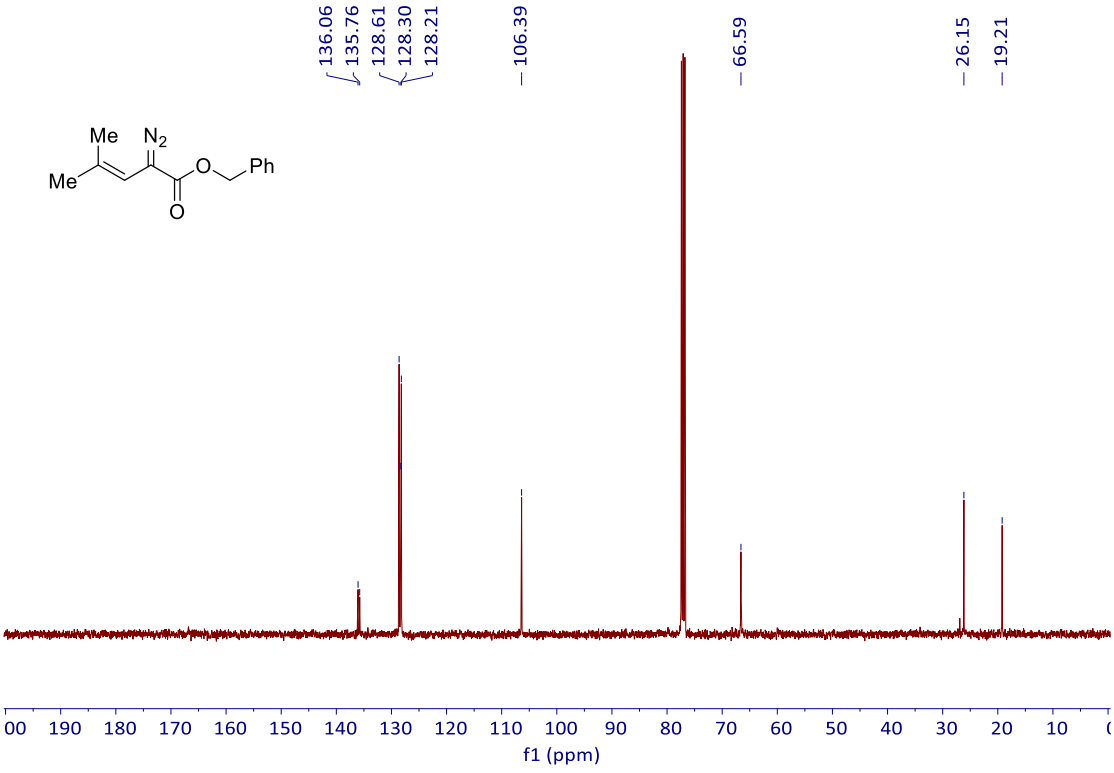
## 8. References


1. Li, W.; Li, S.; Empel, C.; Koenigs, R. M.; Zhou, L., Photoredox-Enabled Self-(3+2) Cyclization of Vinyldiazo Reagents: Synthesis of Cyclopentenyl alpha-Diazo Compounds. *Angew. Chem. Int. Ed.* **2023,** *62* (42), e202309947.
2. Narode, A. S.; Ho, Y.-S.; Cheng, M.-J.; Liu, R.-S., Gold-Catalyzed Addition of β-Oxo Enols at Tethered Alkynes via a Non-Conia-ene Pathway: Observation of a Formal 1,3-Hydroxymethylidene Migration. *Org. Lett.* **2023,** *25* (9), 1589-1594.
3. Li, S.; Zhou, L., Photocatalytic (3 + 3) Annnulation of Vinyldiazo Compounds and Aminocyclopropanes. *Org. Lett.* **2024,** *26* (15), 3294-3298.
4. Chen, X.; Gao, Y.; Yu, S.; Liang, J.; Zhou, L., Lewis-Acid-Catalyzed Diastereoselective [4 + 2] Cycloaddition of Vinyldiazo Compounds with N-Acyliminium Cations. *Org. Lett.* **2025,** *27* (10), 2515-2520.
5. Qin, C.; Davies, H. M. L., Silver-Catalyzed Vinylogous Fluorination of Vinyl Diazoacetates. *Org. Lett.* **2013,** *15* (24), 6152-6154.

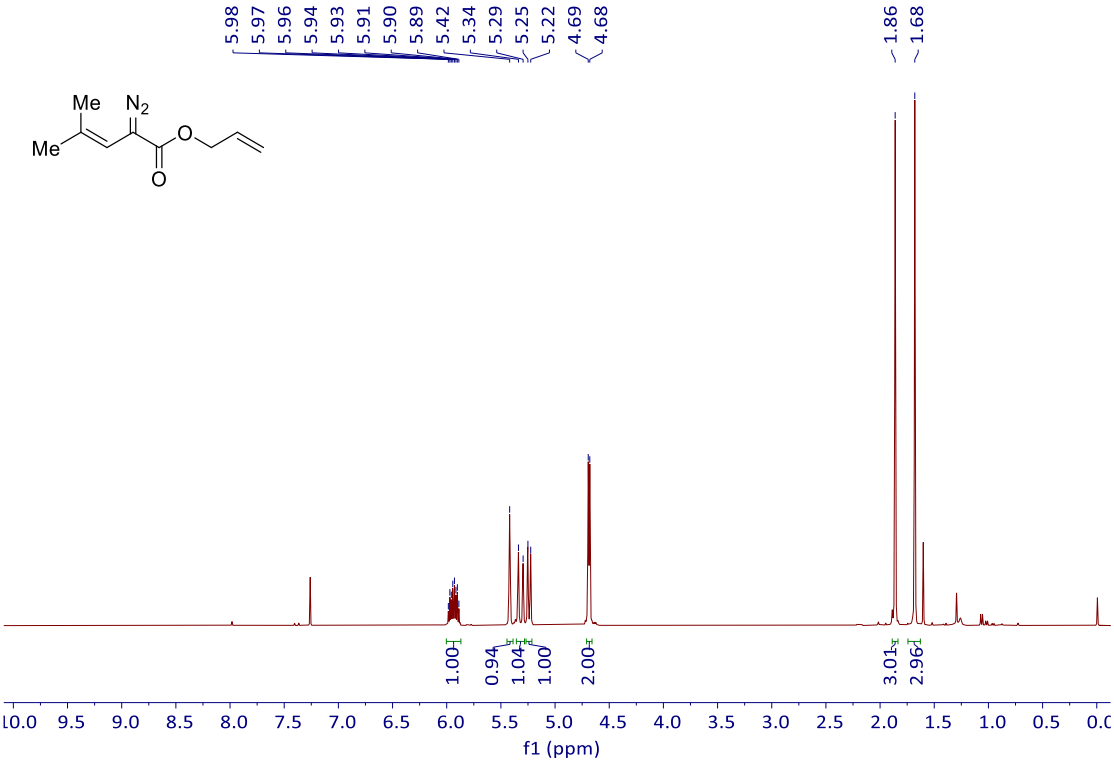
## 9. Copies of $^{1}$H NMR and $^{13}$C NMR spectra of substances and products



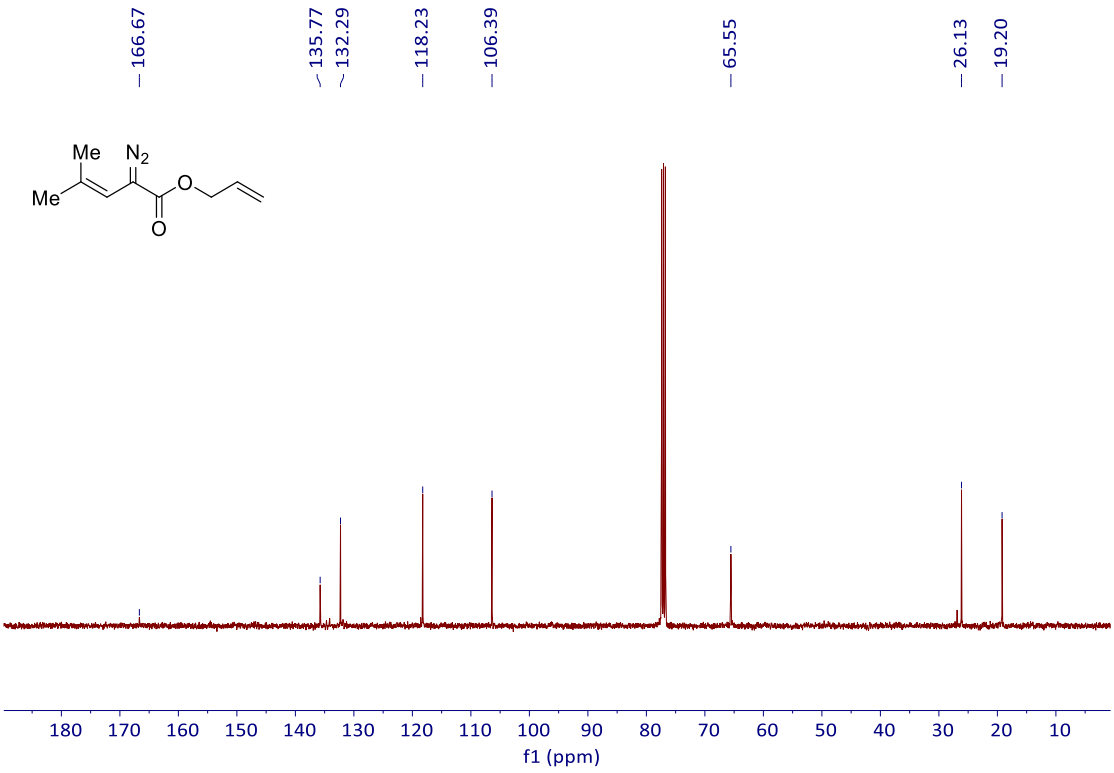

$^{1}$H NMR of **1a** (400 Hz, $CDCl_3$)



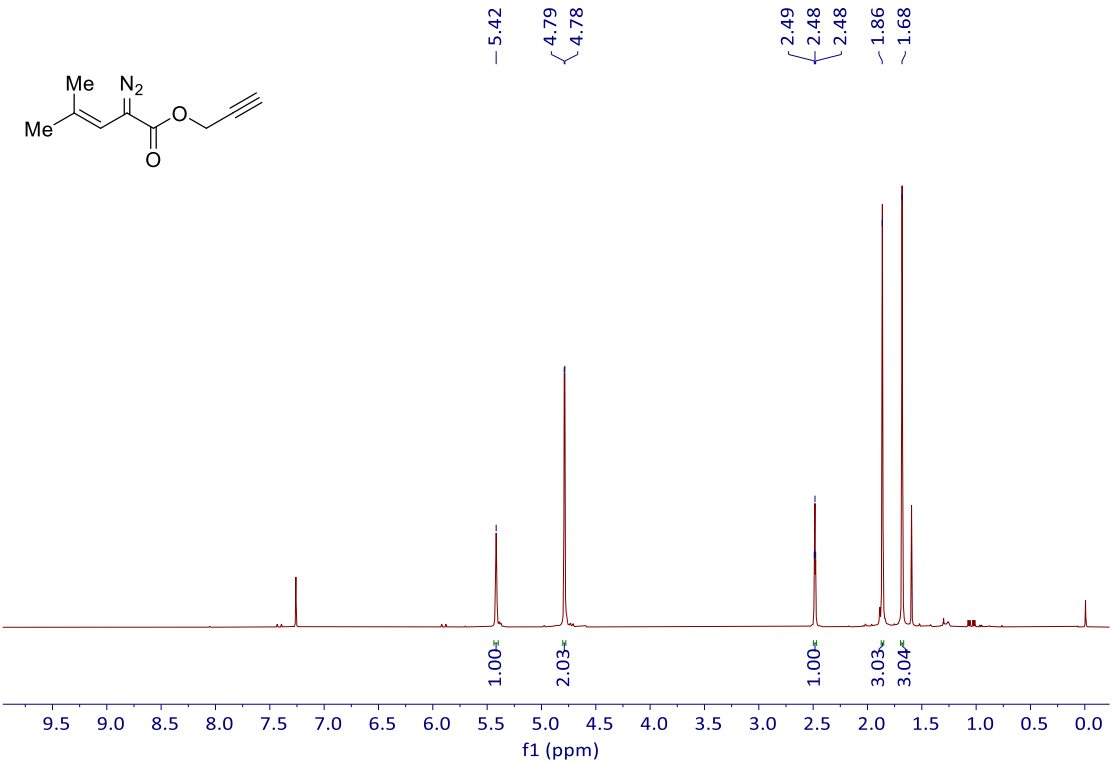

$^{13}$C NMR of **1a** (100 Hz, $CDCl_3$)



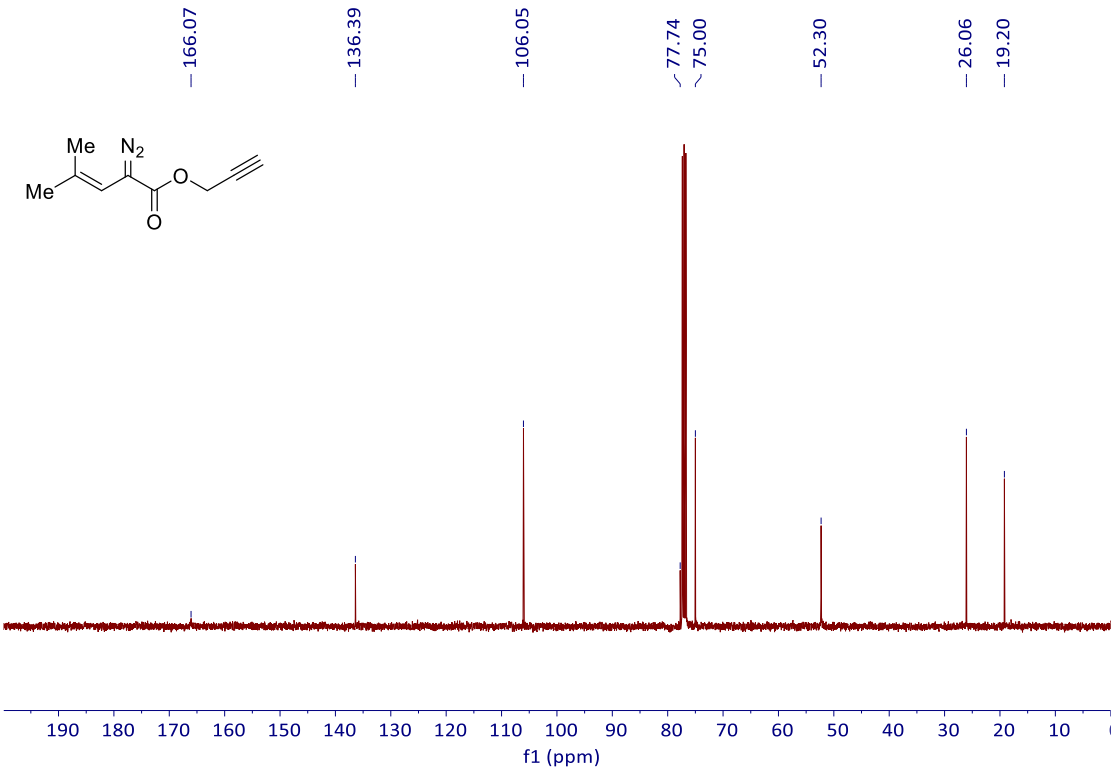

$^{1}$H NMR of **1b** (400 Hz, $CDCl_3$)



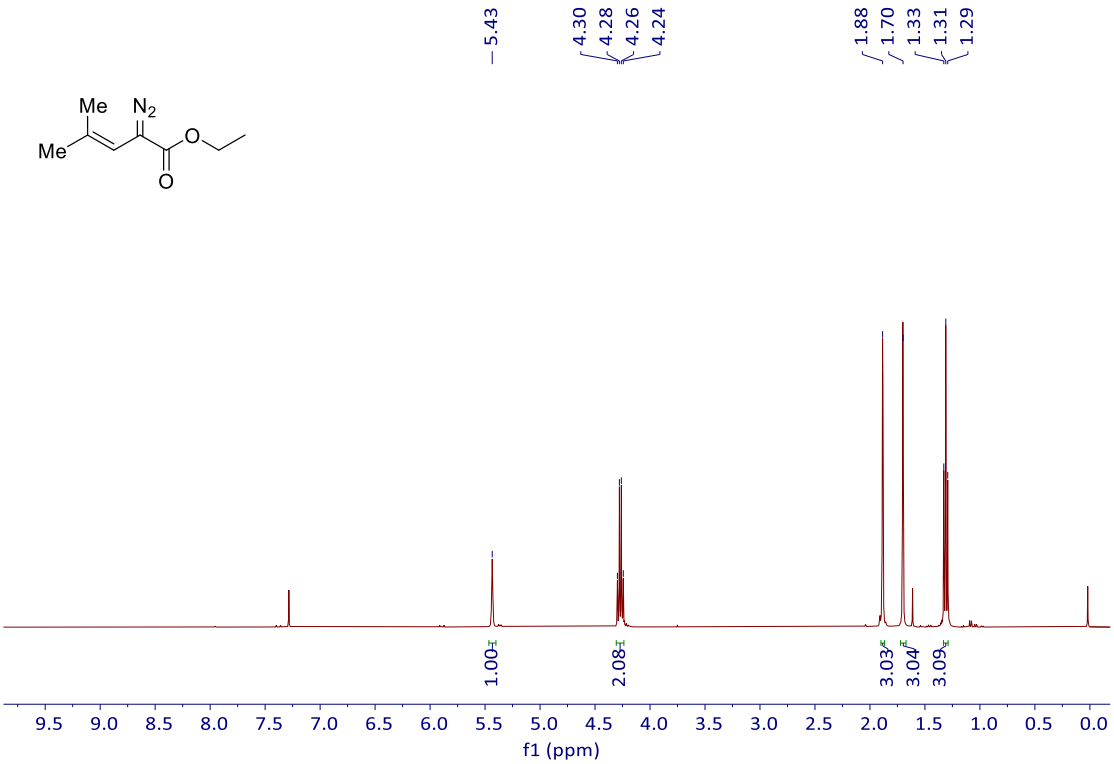

$^{13}$C NMR of **1b** (100 Hz, $CDCl_3$)



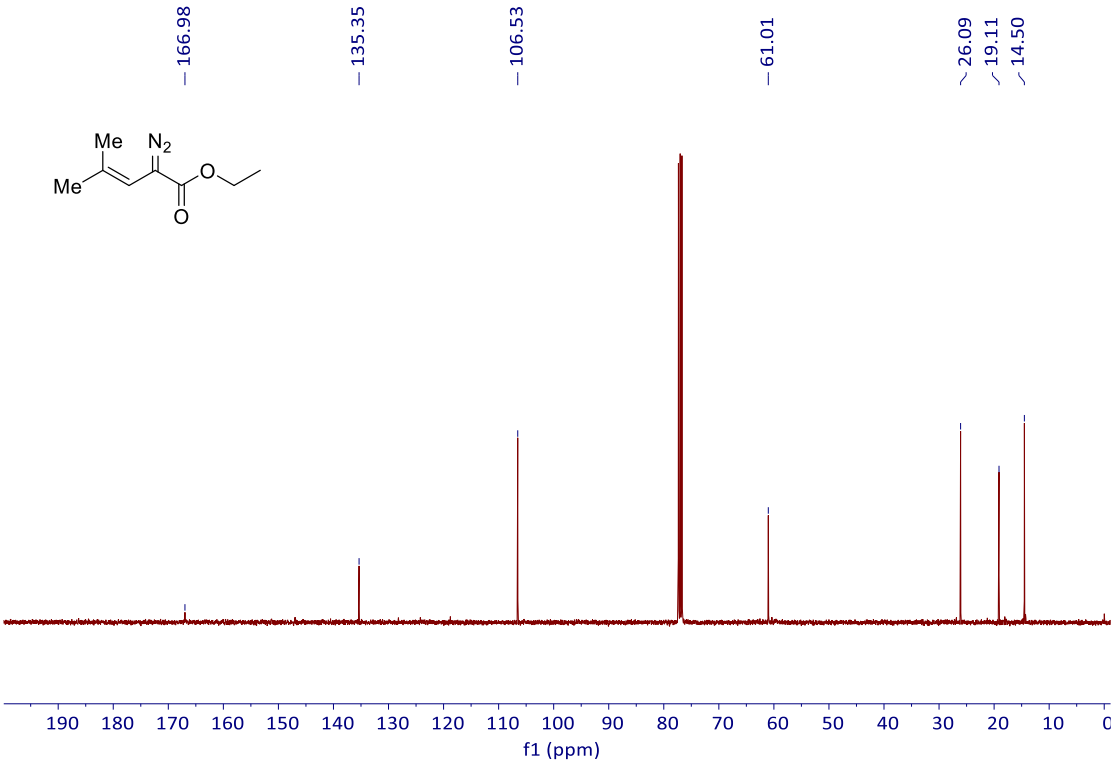

$^{1}$H NMR of **1c** (400 Hz, $CDCl_3$)



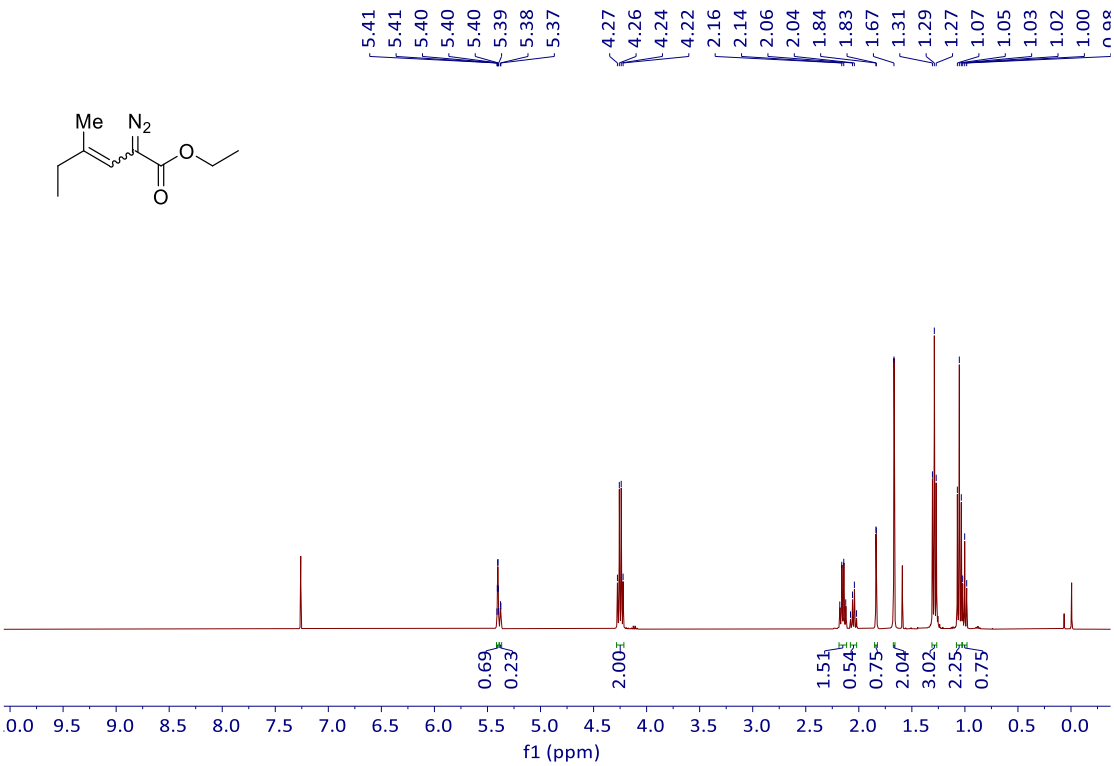

$^{13}$C NMR of **1c** (100 Hz, $CDCl_3$)



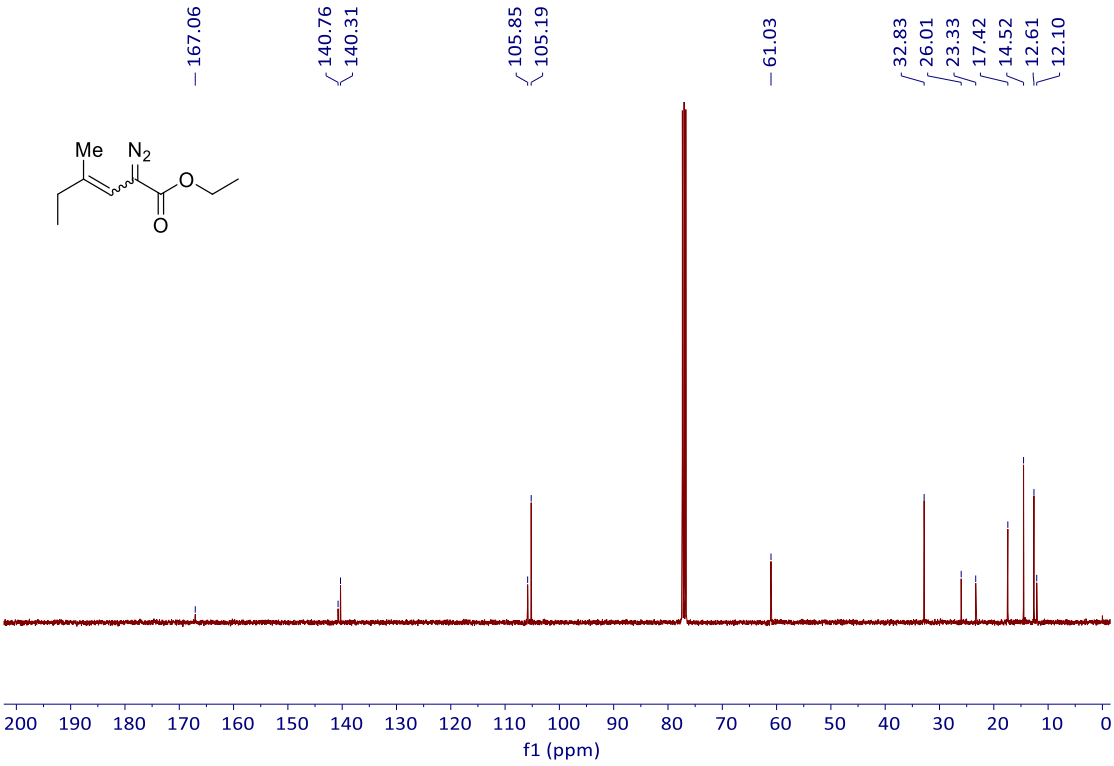

$^{1}$H NMR of **1d** (400 Hz, $CDCl_3$)



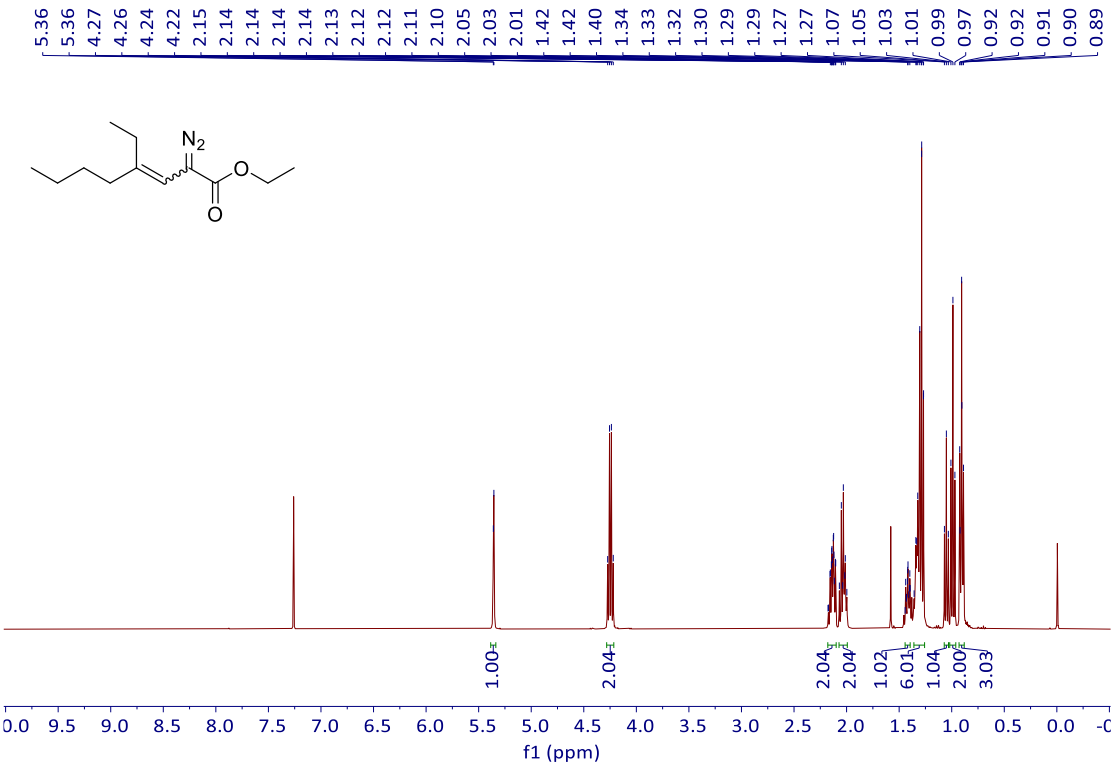

$^{13}$C NMR of **1d** (100 Hz, $CDCl_3$)



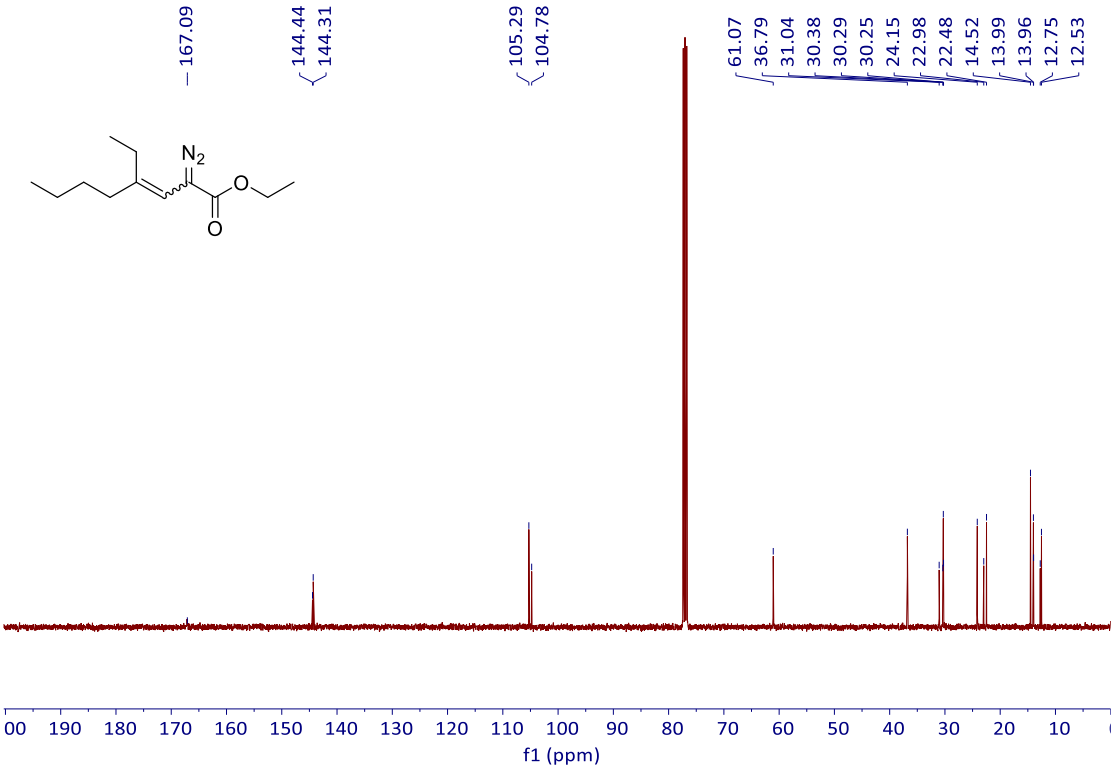

$^{1}$H NMR of **1e** (400 Hz, $CDCl_3$)



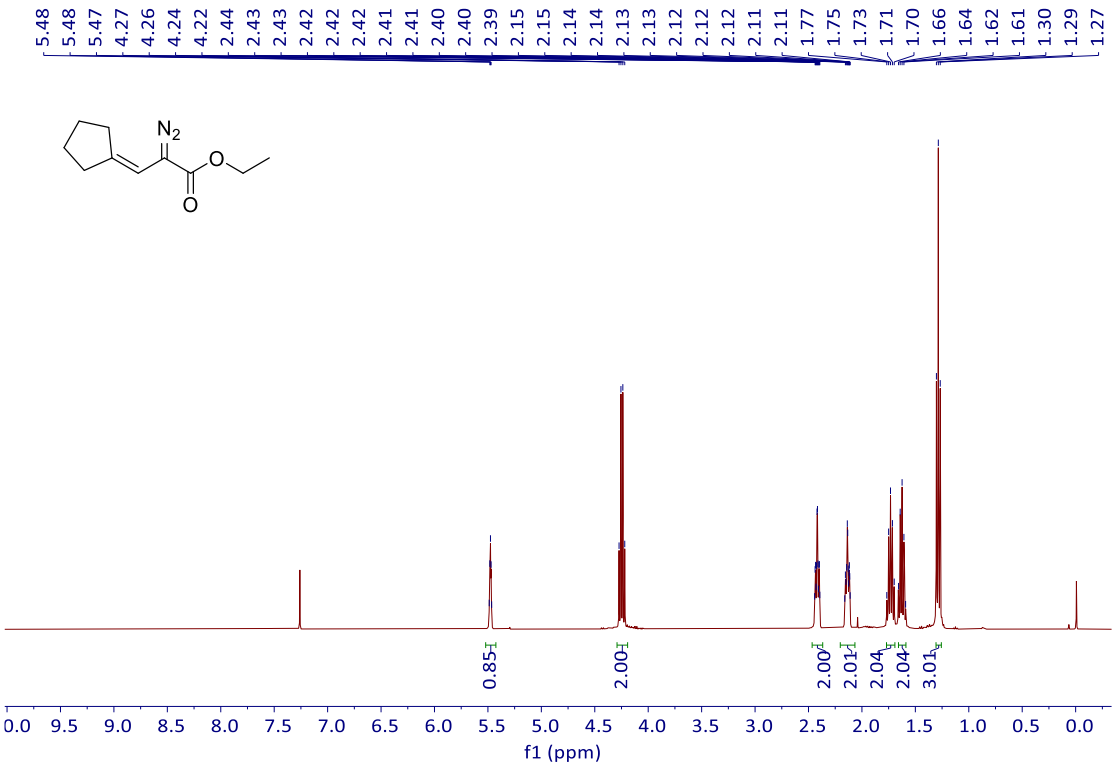

$^{13}$C NMR of **1e** (100 Hz, $CDCl_3$)



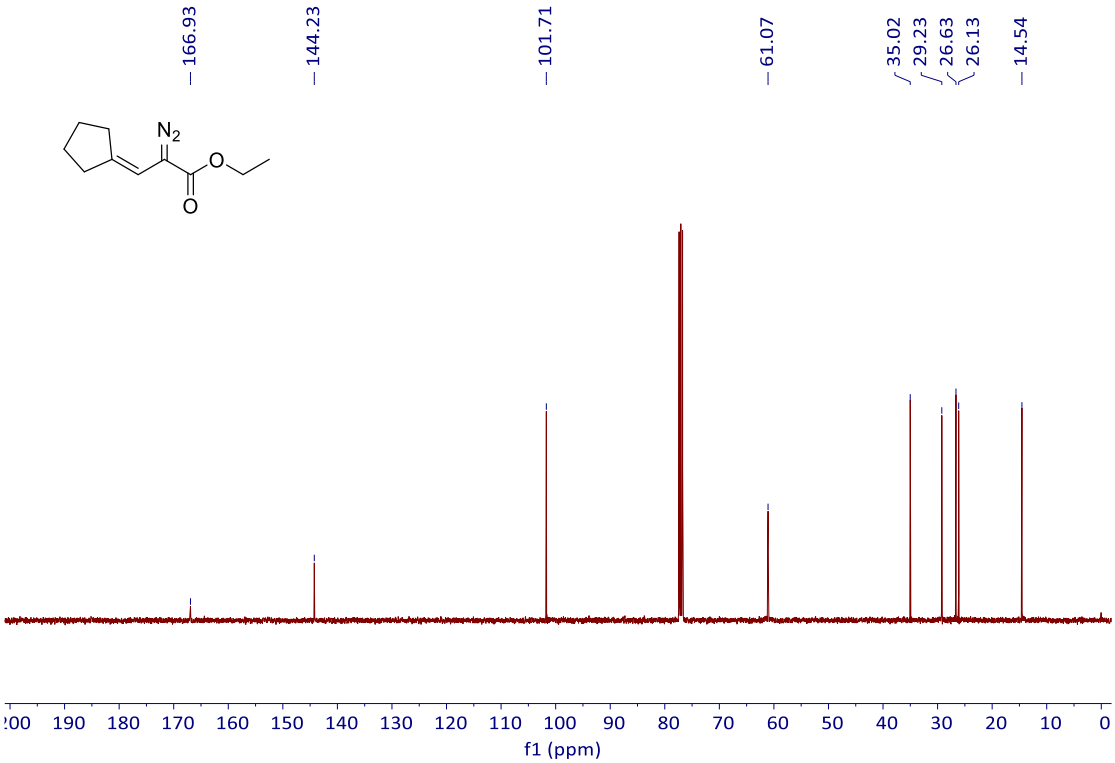

$^{1}$H NMR of **1f** (400 Hz, $CDCl_3$)



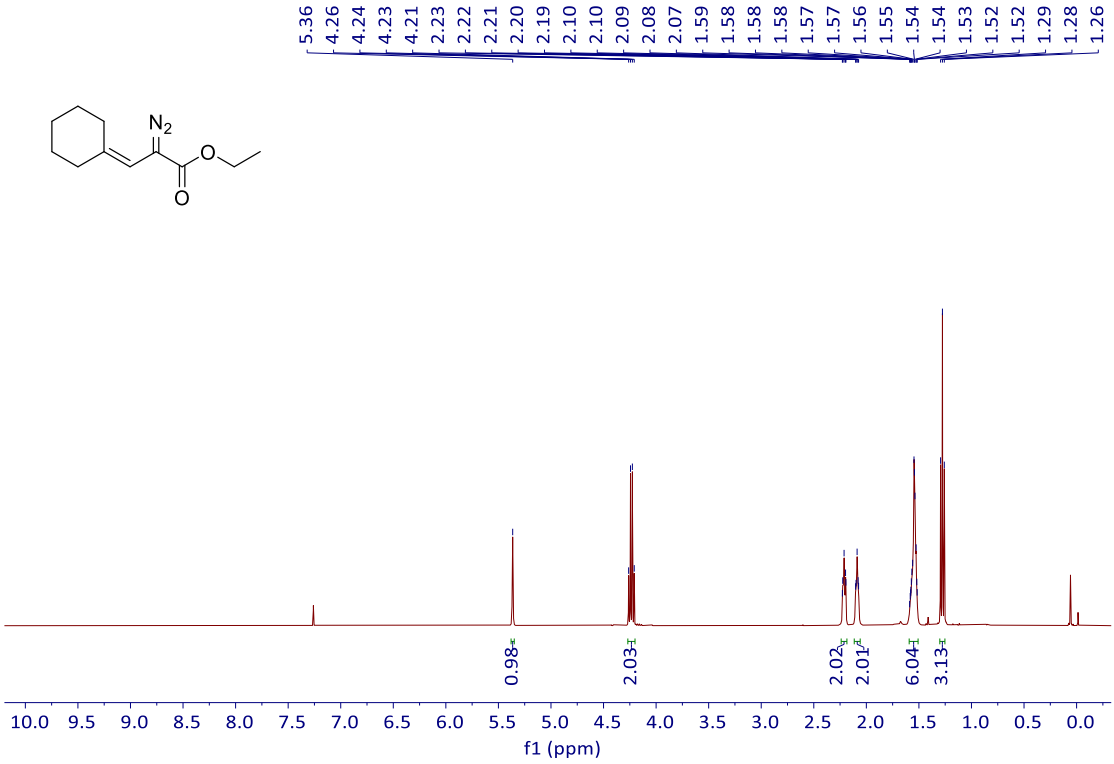

$^{13}$C NMR of **1f** (100 Hz, $CDCl_3$)



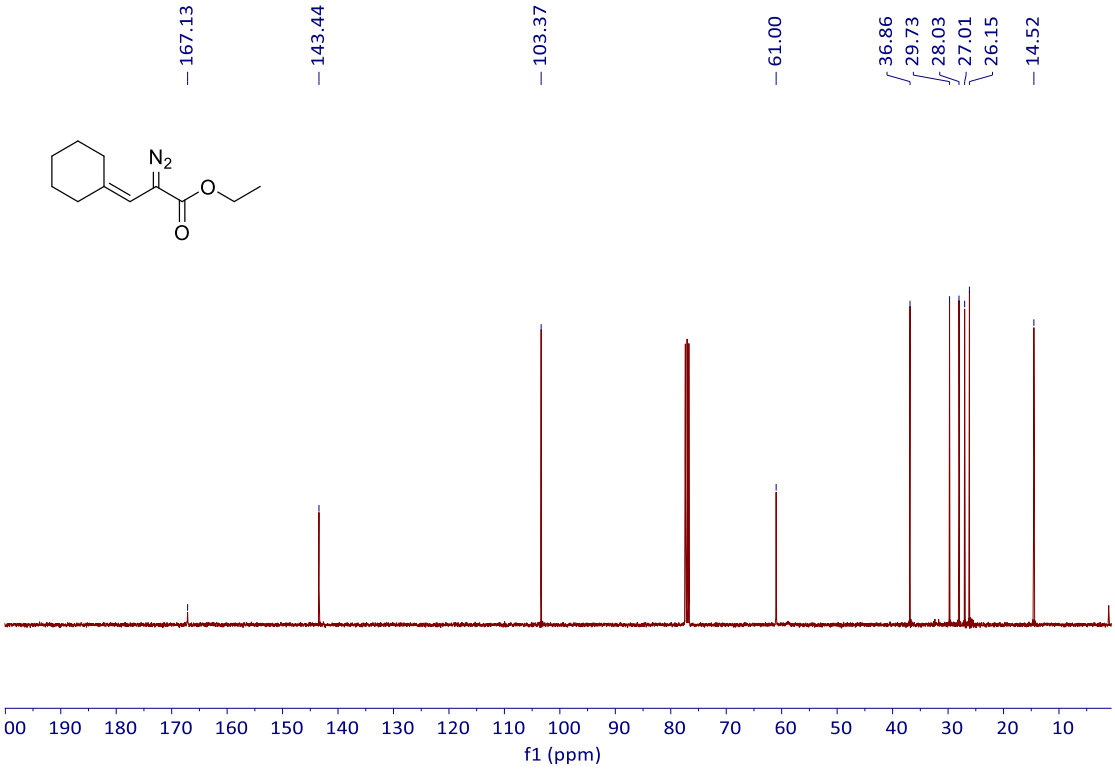

$^{1}$H NMR of **1g** (400 Hz, $CDCl_3$)



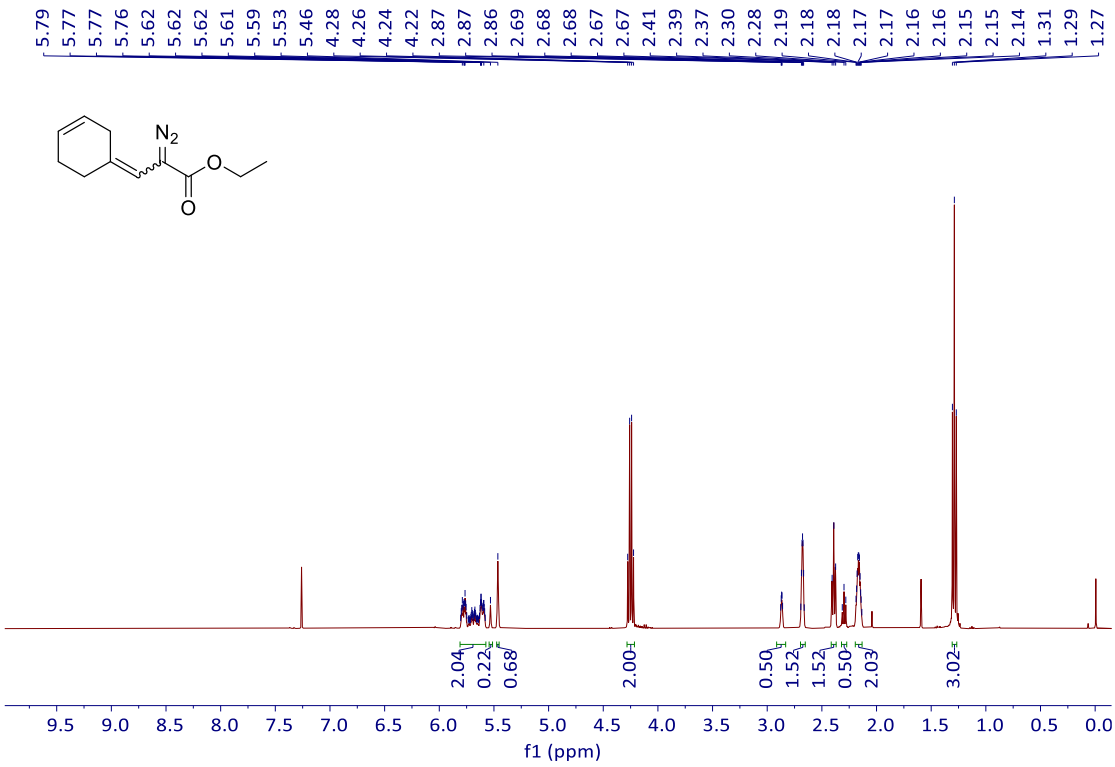

$^{13}$C NMR of **1g** (100 Hz, $CDCl_3$)



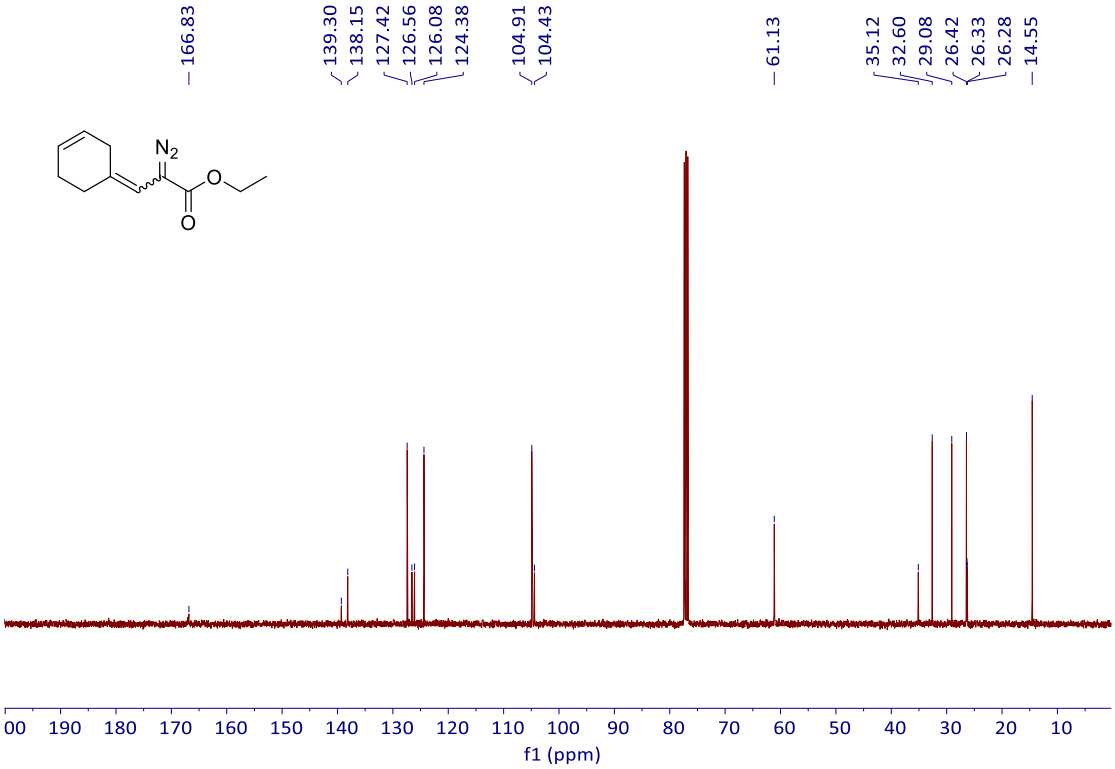

$^{1}$H NMR of **1h** (400 Hz, $CDCl_3$)



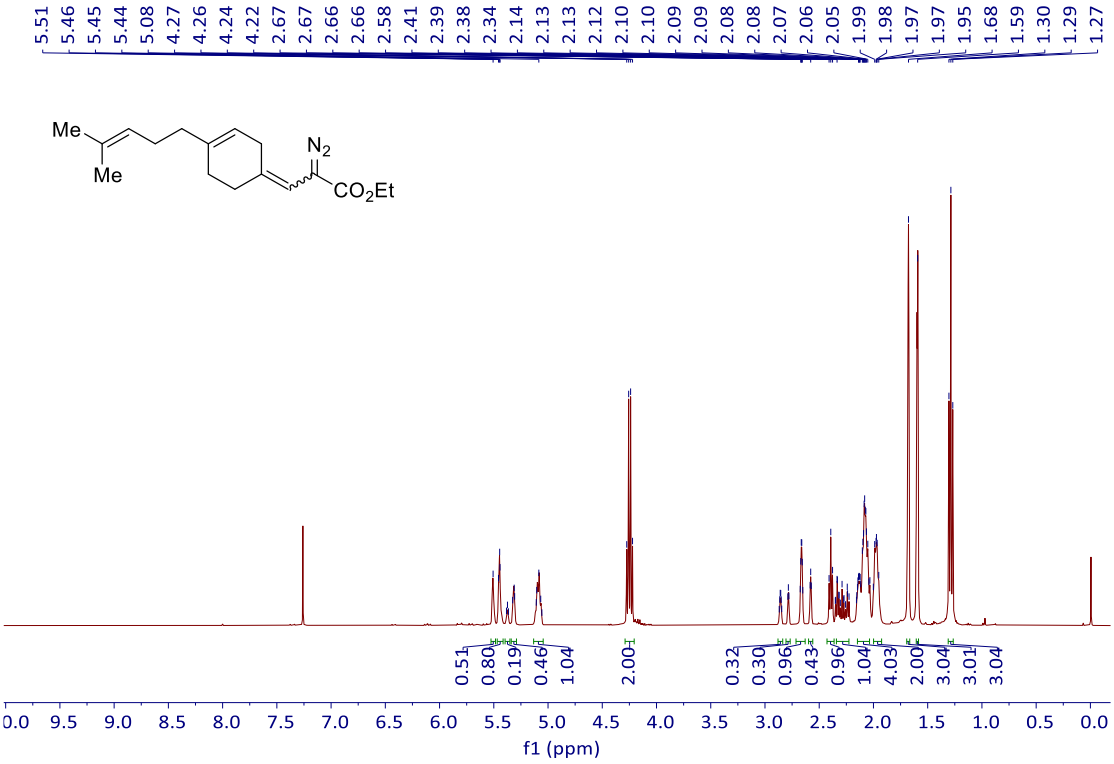

$^{13}$C NMR of **1h** (100 Hz, $CDCl_3$)



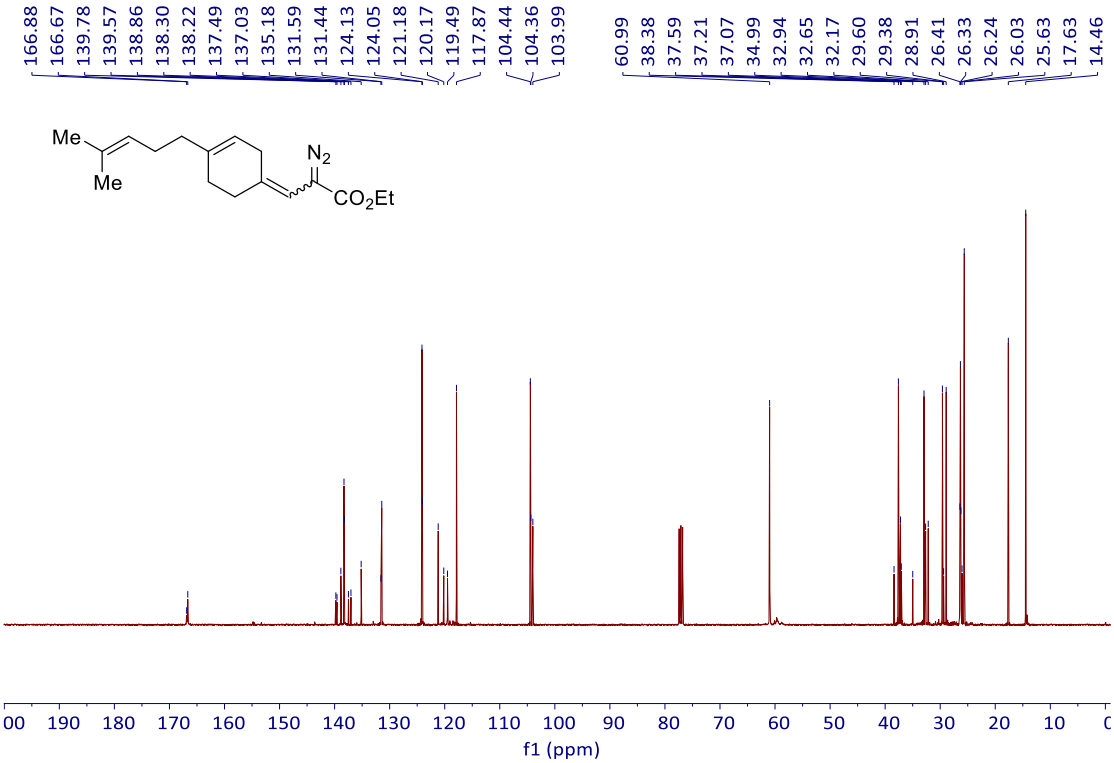

$^{1}$H NMR of **1i** (400 Hz, $CDCl_3$)



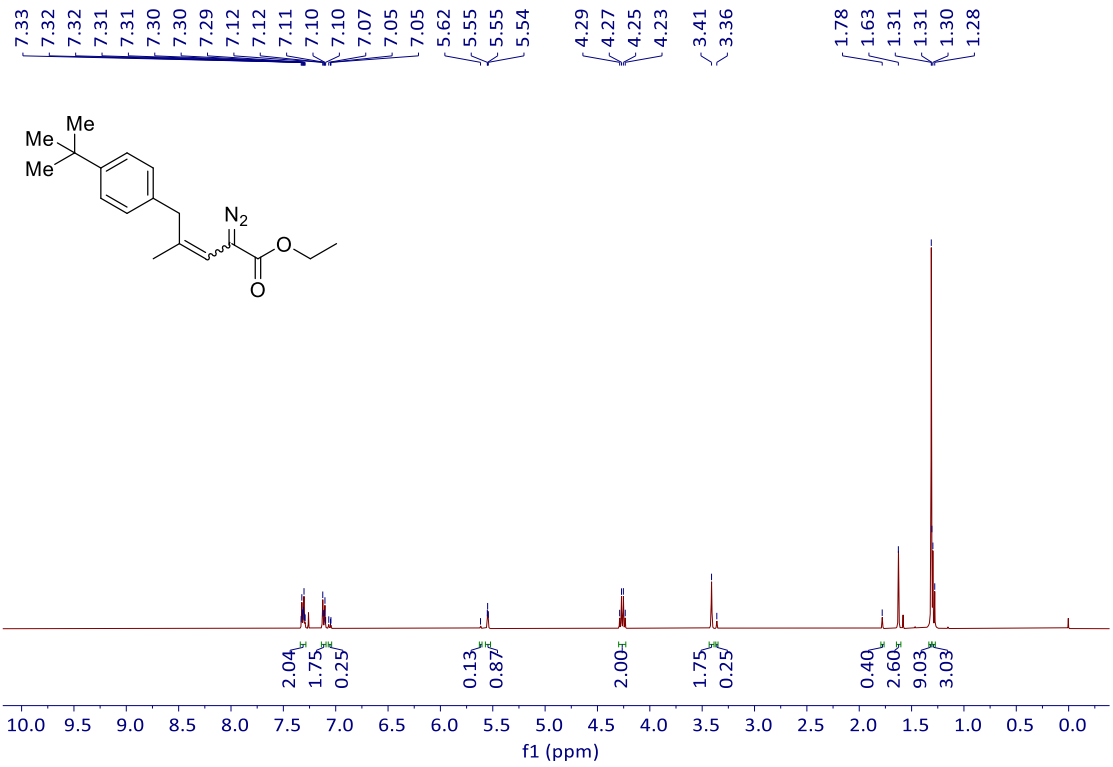

$^{13}$C NMR of **1i** (100 Hz, $CDCl_3$)



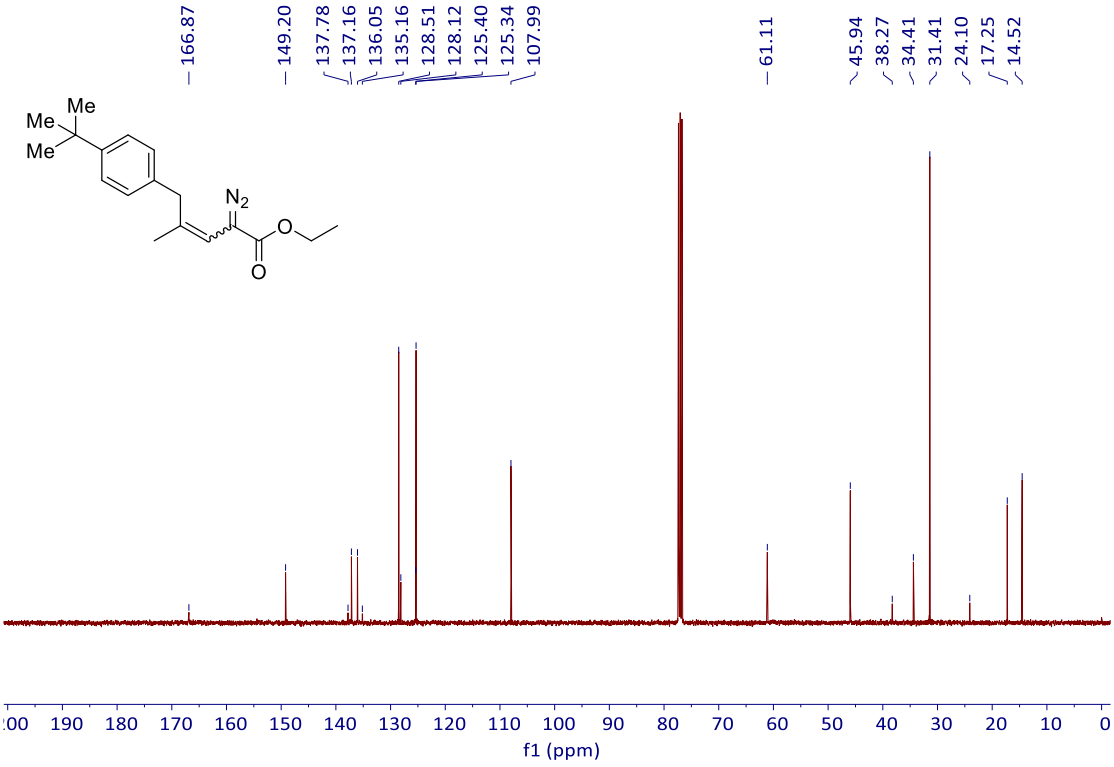

$^{1}$H NMR of **1j** (400 Hz, $CDCl_3$)



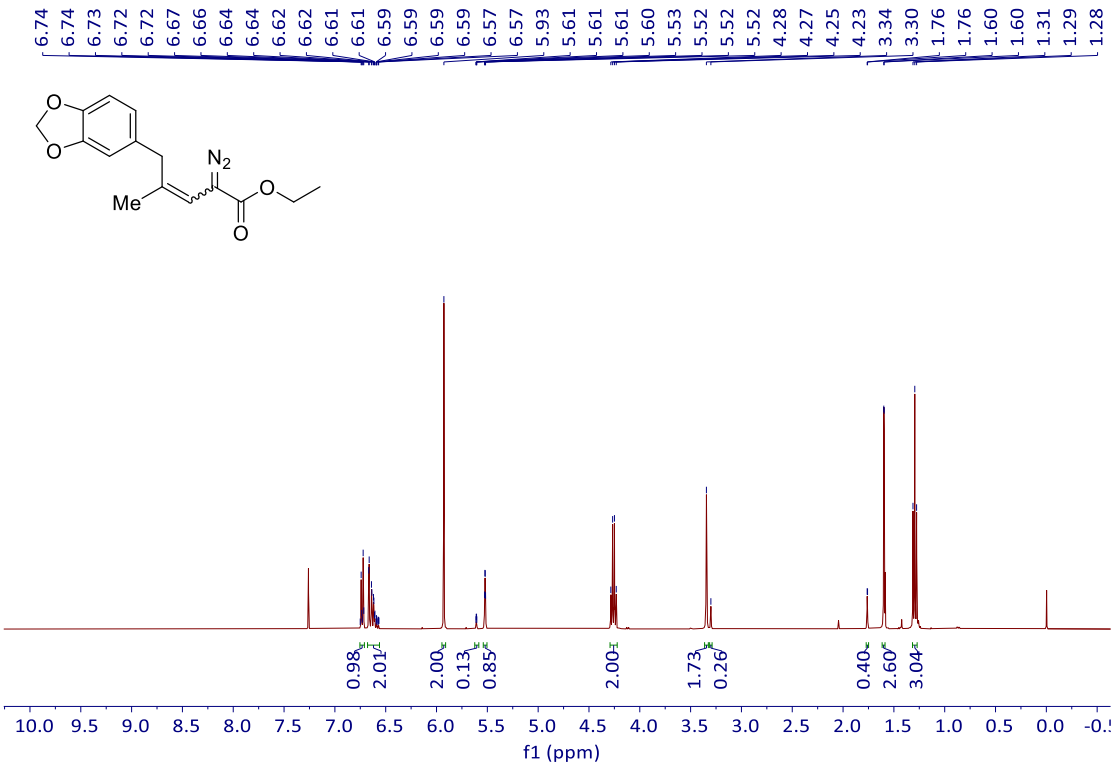

$^{13}$C NMR of **1j**(100 Hz, $CDCl_3$)



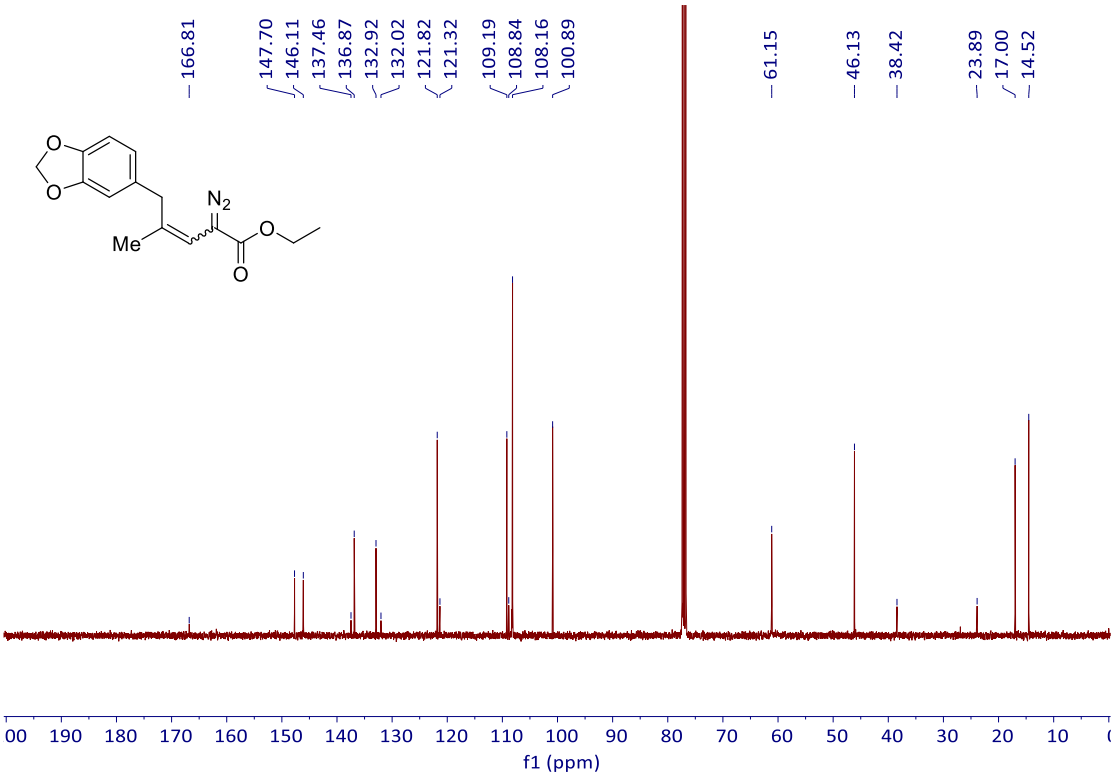

$^{1}$H NMR of **1k** (400 Hz, $CDCl_3$)



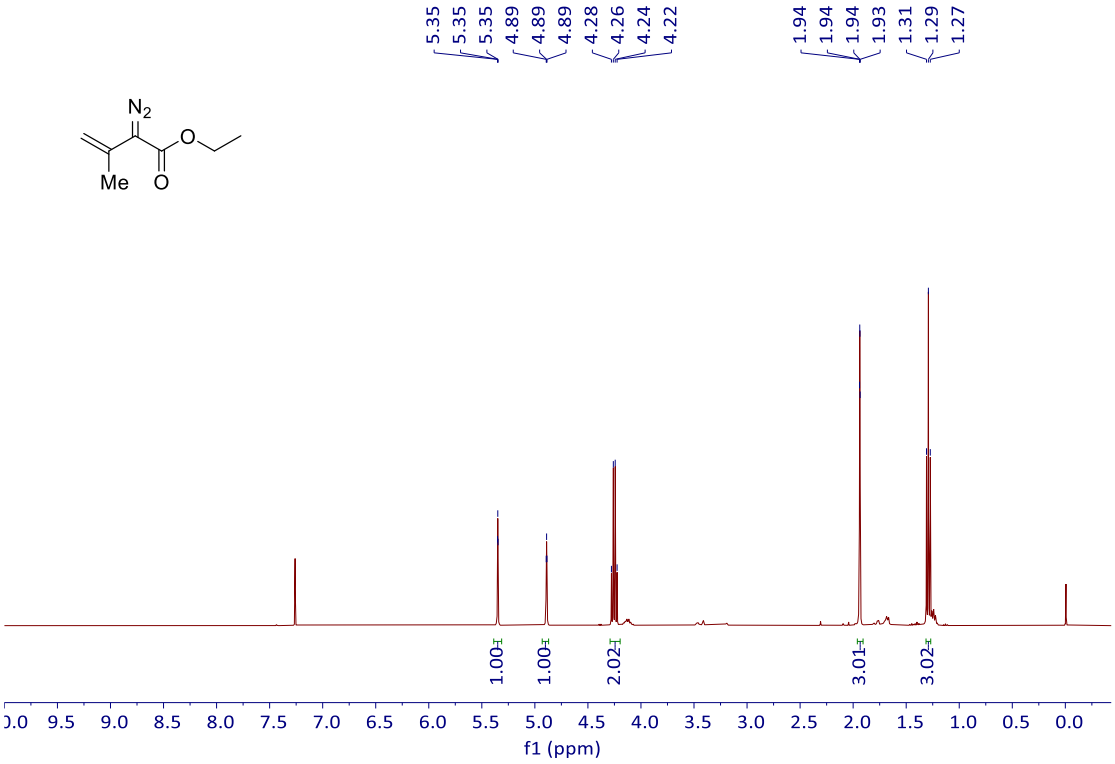

$^{13}$C NMR of **1k** (100 Hz, $CDCl_3$)



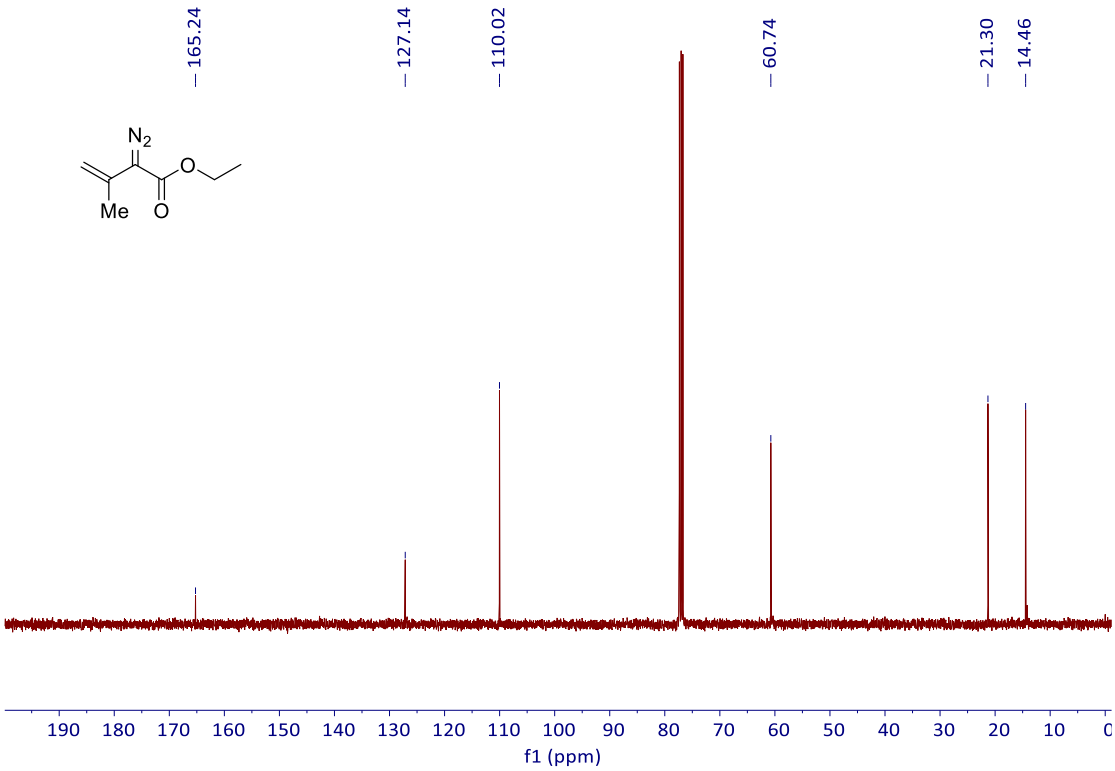

$^{1}$H NMR of **1l** (400 Hz, $CDCl_3$)



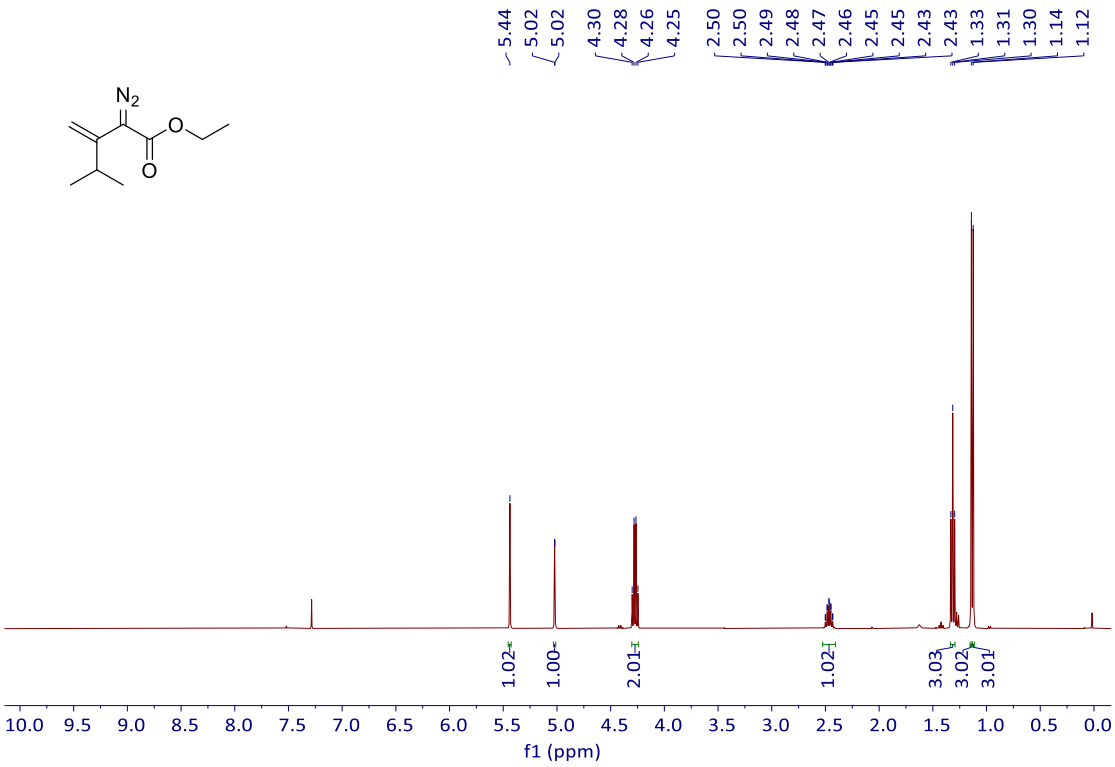

$^{13}$C NMR of **1l** (100 Hz, $CDCl_3$)



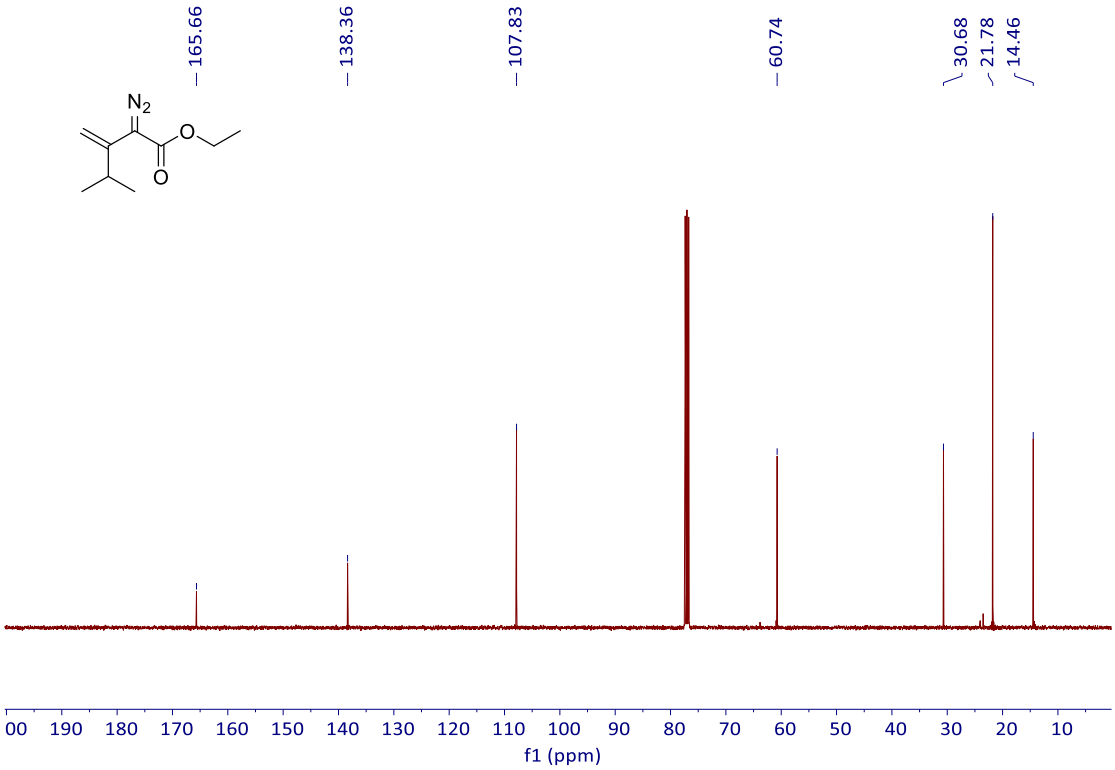

$^{1}$H NMR of **1m**(400 Hz, $CDCl_3$)



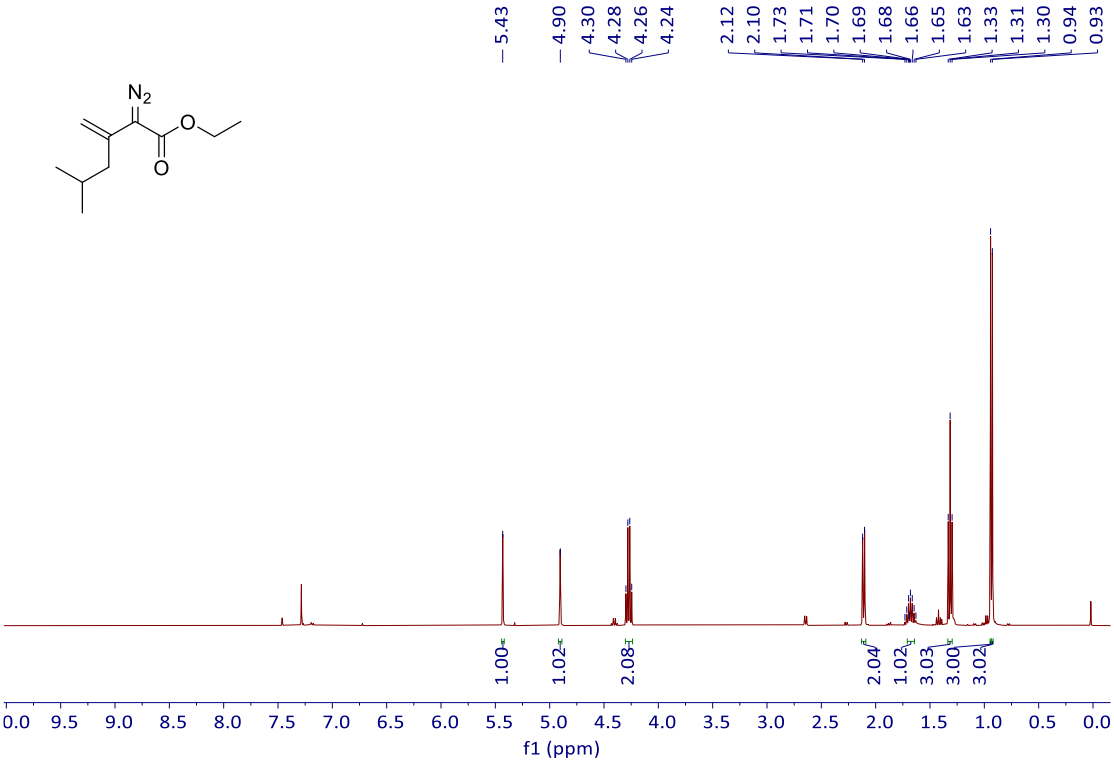

$^{13}$C NMR of **1m** (100 Hz, $CDCl_3$)



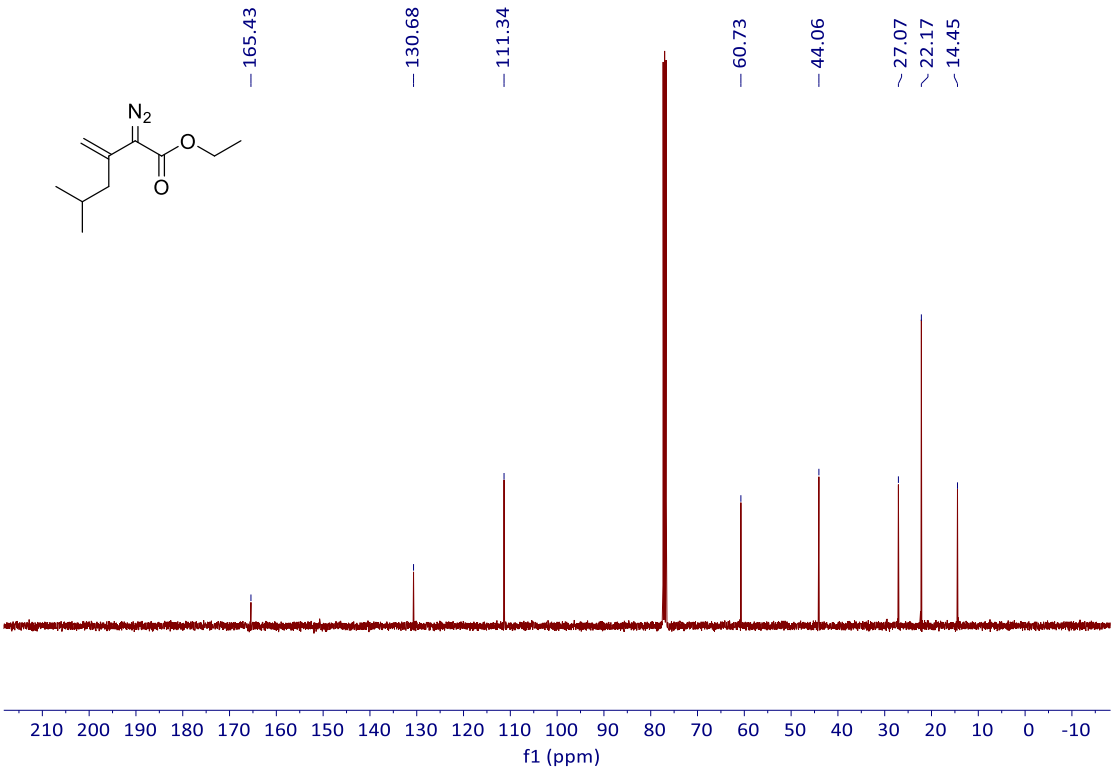

$^{1}$H NMR of **1n** (400 Hz, $CDCl_3$)



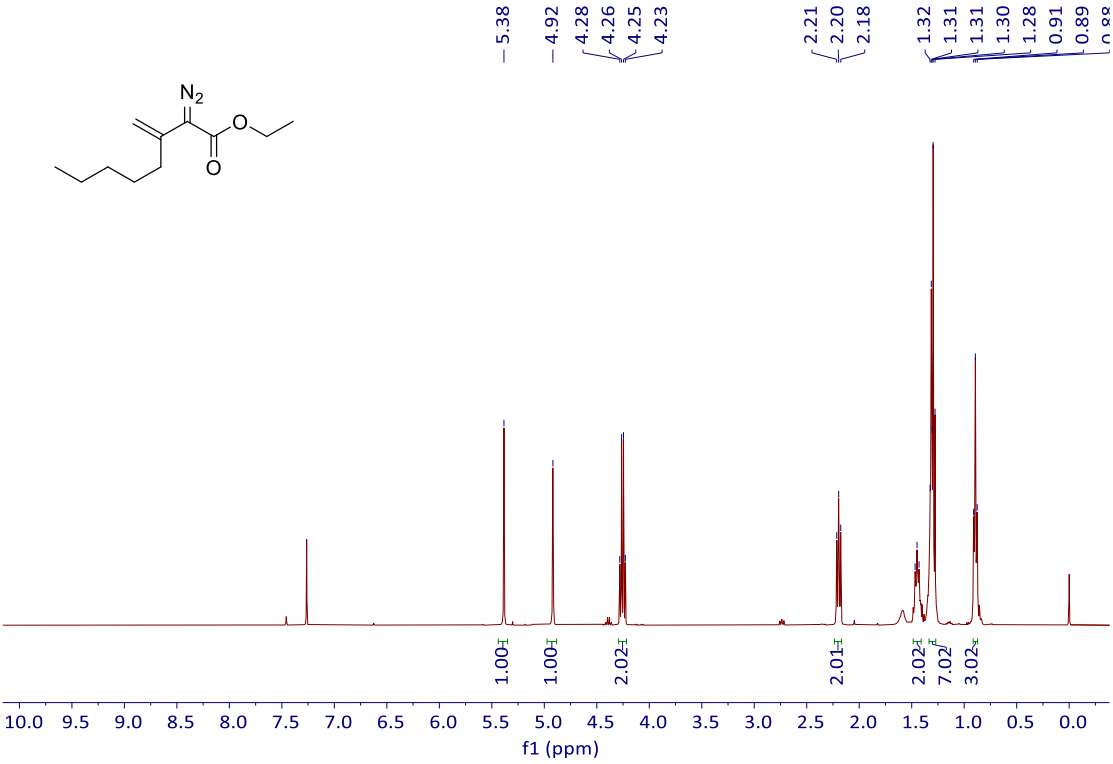

$^{13}$C NMR of **1n** (100 Hz, $CDCl_3$)



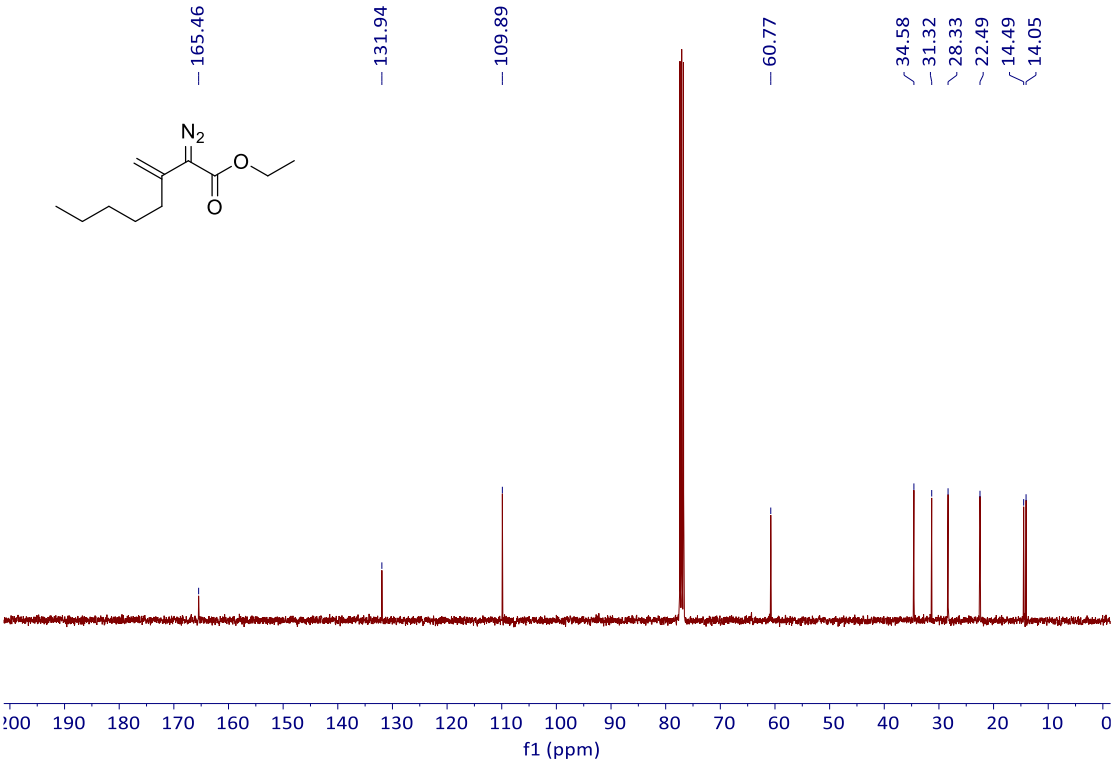

$^{1}$H NMR of **1o** (400 Hz, $CDCl_3$)



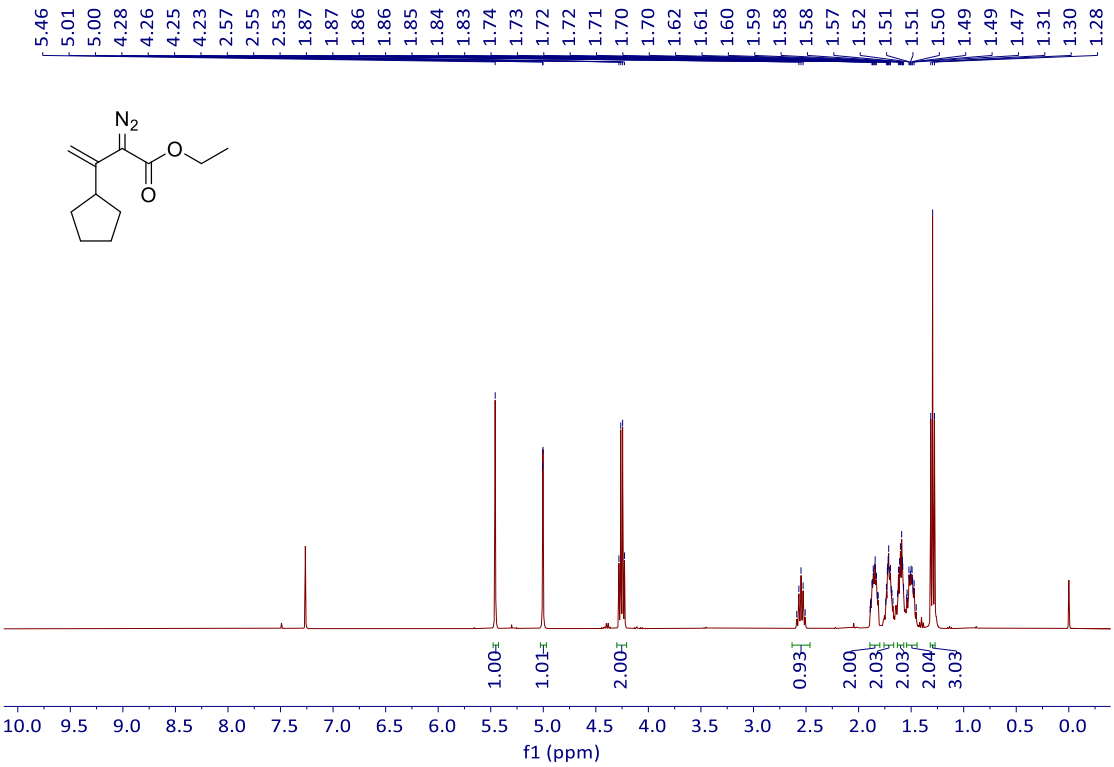

$^{13}$C NMR of **1o** (100 Hz, $CDCl_3$)



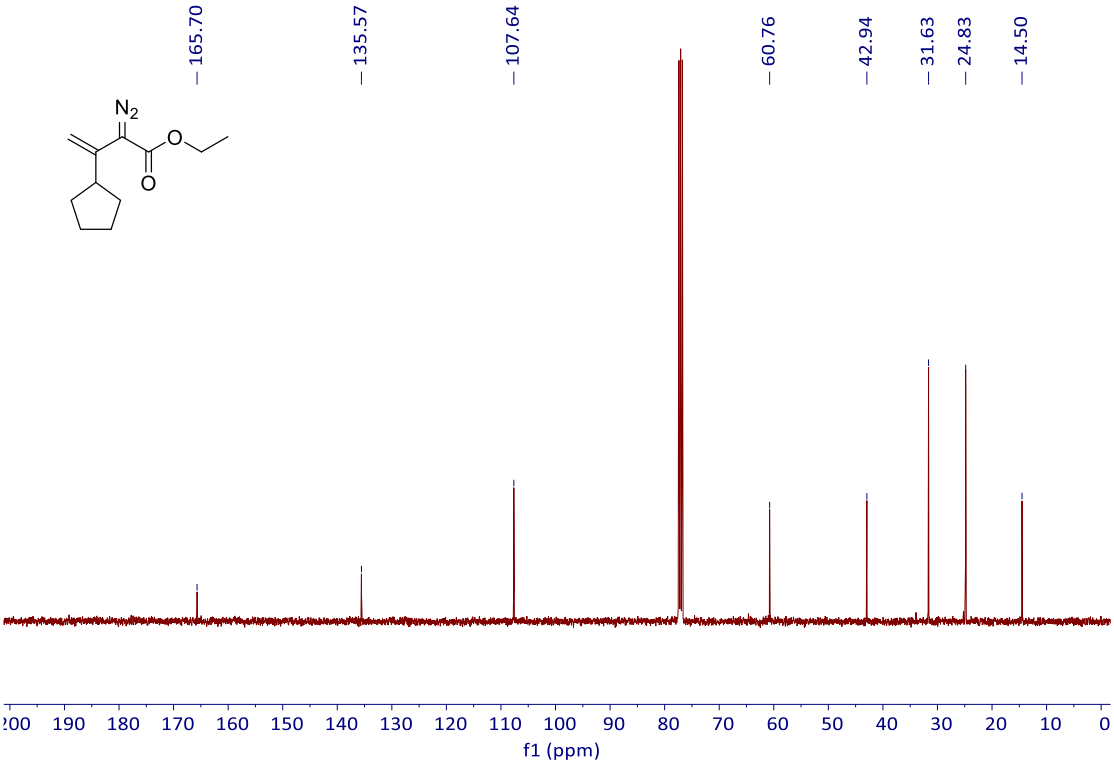

$^{1}$H NMR of **1p** (400 Hz, $CDCl_3$)



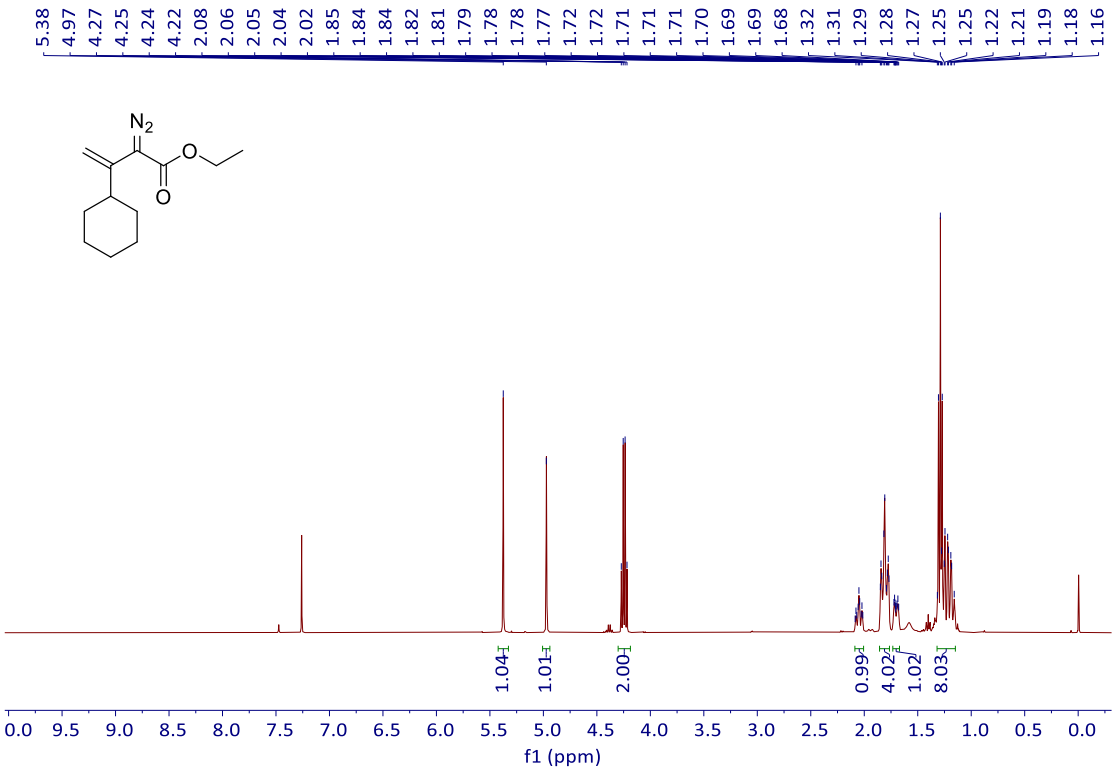

$^{13}$C NMR of **1p** (100 Hz, $CDCl_3$)



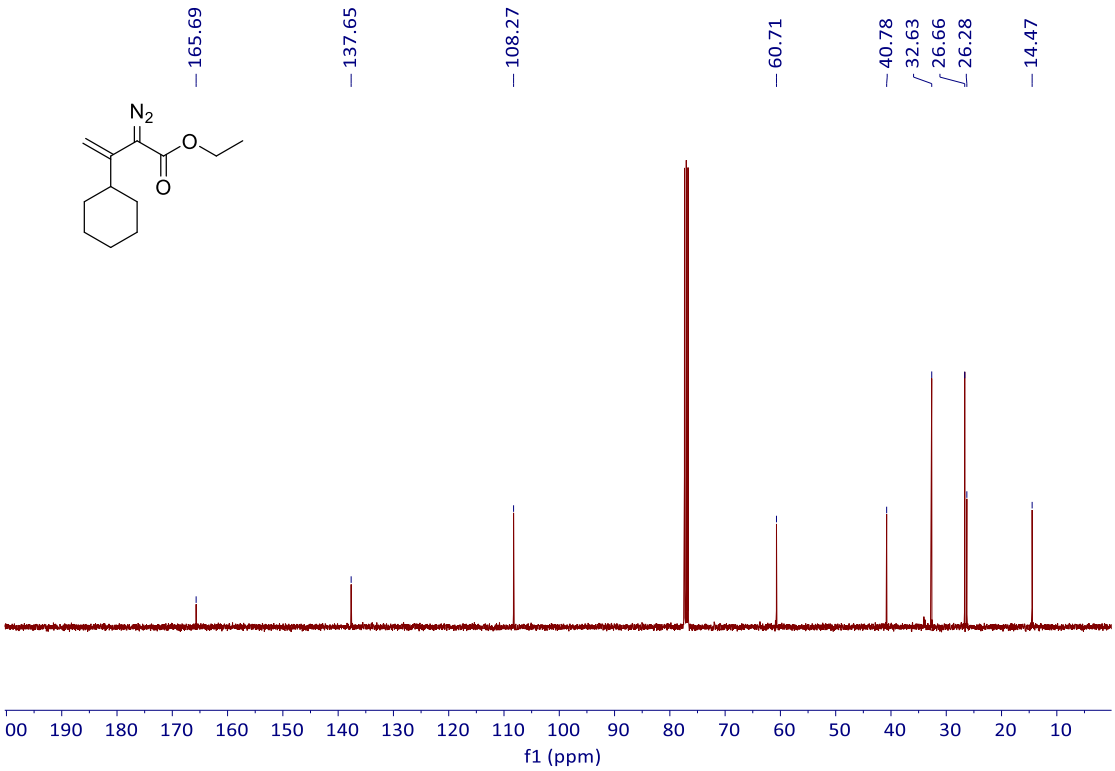

$^{1}$H NMR of **1q** (400 Hz, $CDCl_3$)



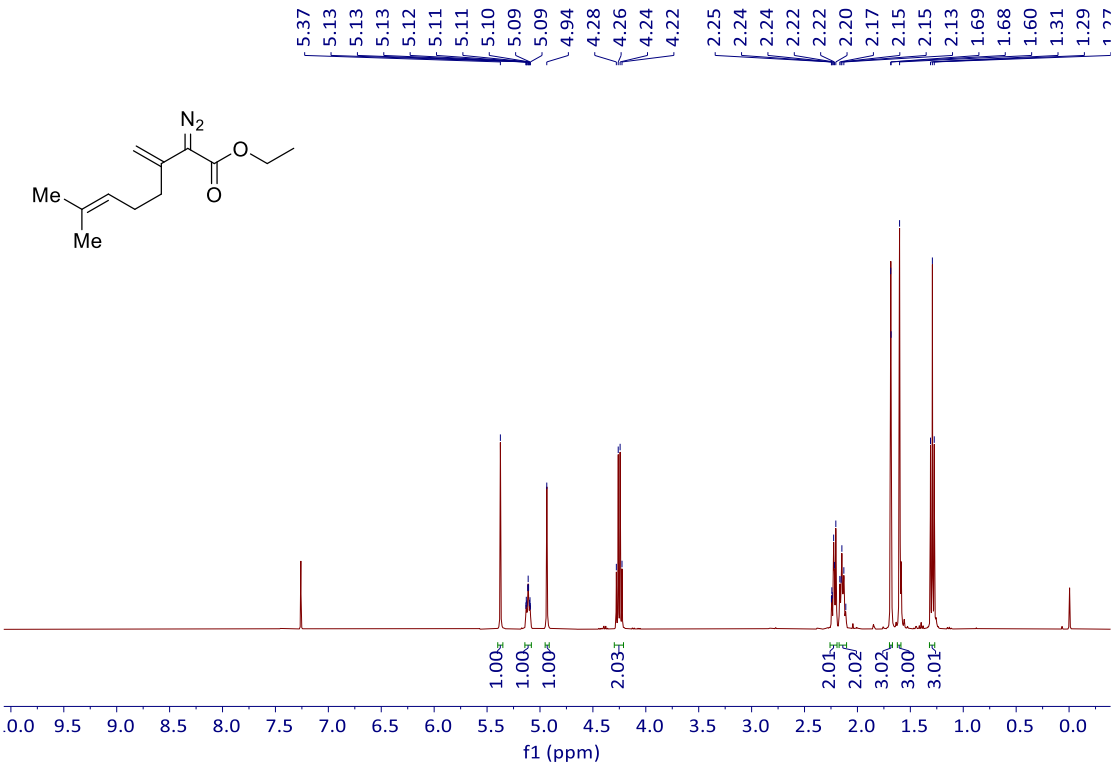

$^{13}$C NMR of **1q** (100 Hz, $CDCl_3$)



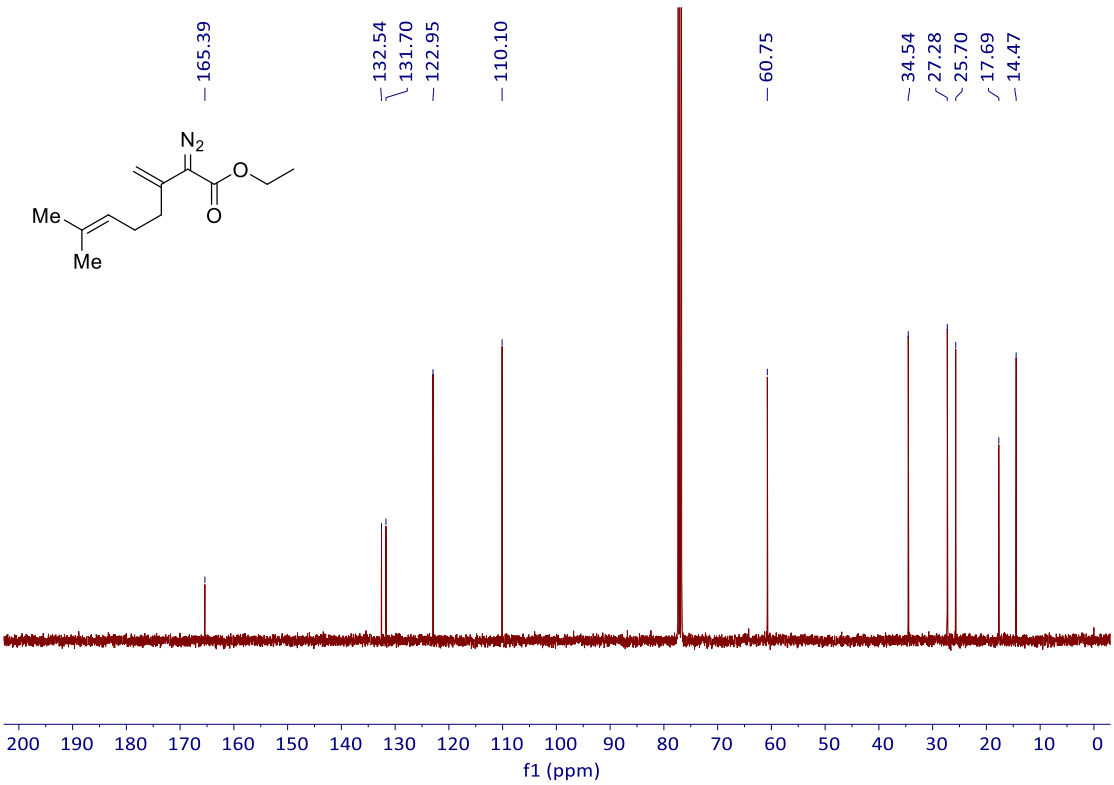

$^{1}$H NMR of **1r** (400 Hz, $CDCl_3$)



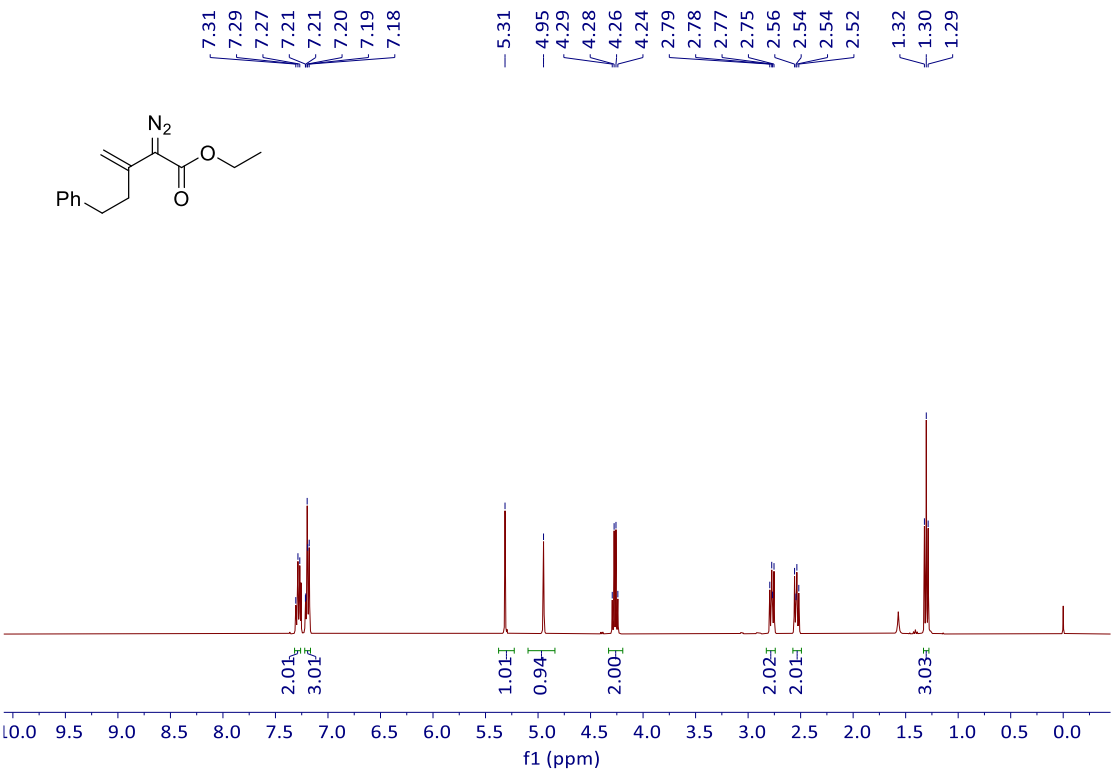

$^{13}$C NMR of **1r**(100 Hz, $CDCl_3$)



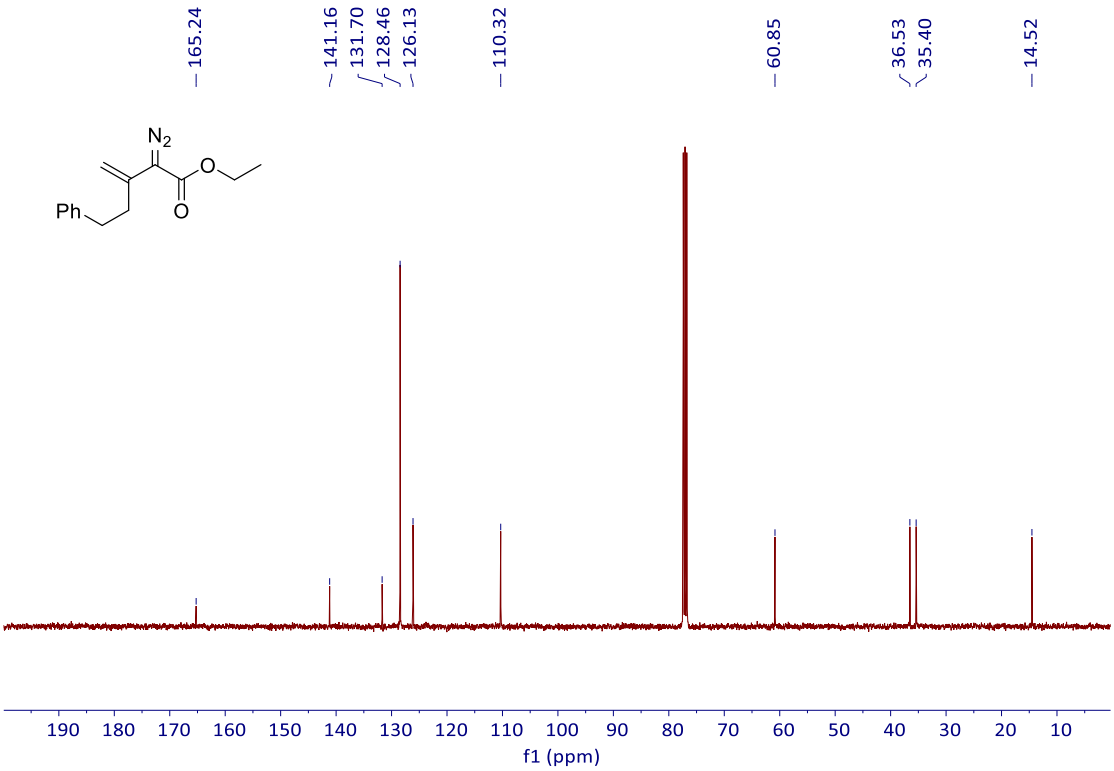

$^{1}$H NMR of **1s** (400 Hz, $CDCl_3$)



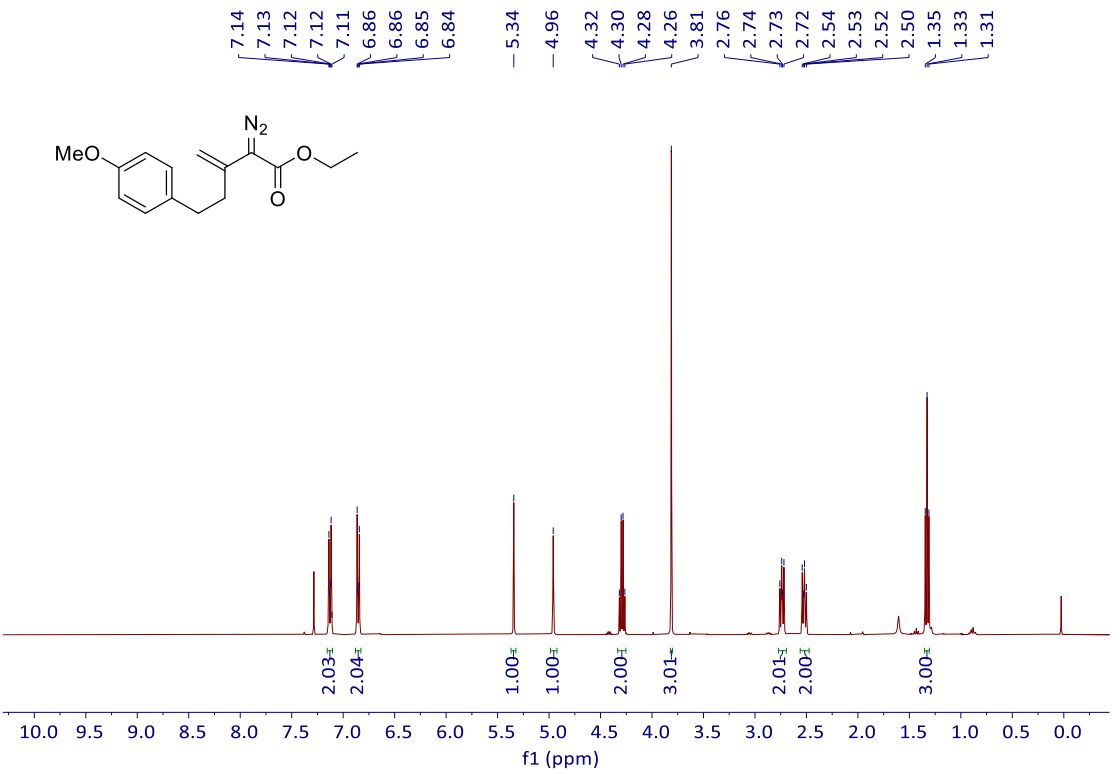

$^{13}$C NMR of **1s** (100 Hz, $CDCl_3$)



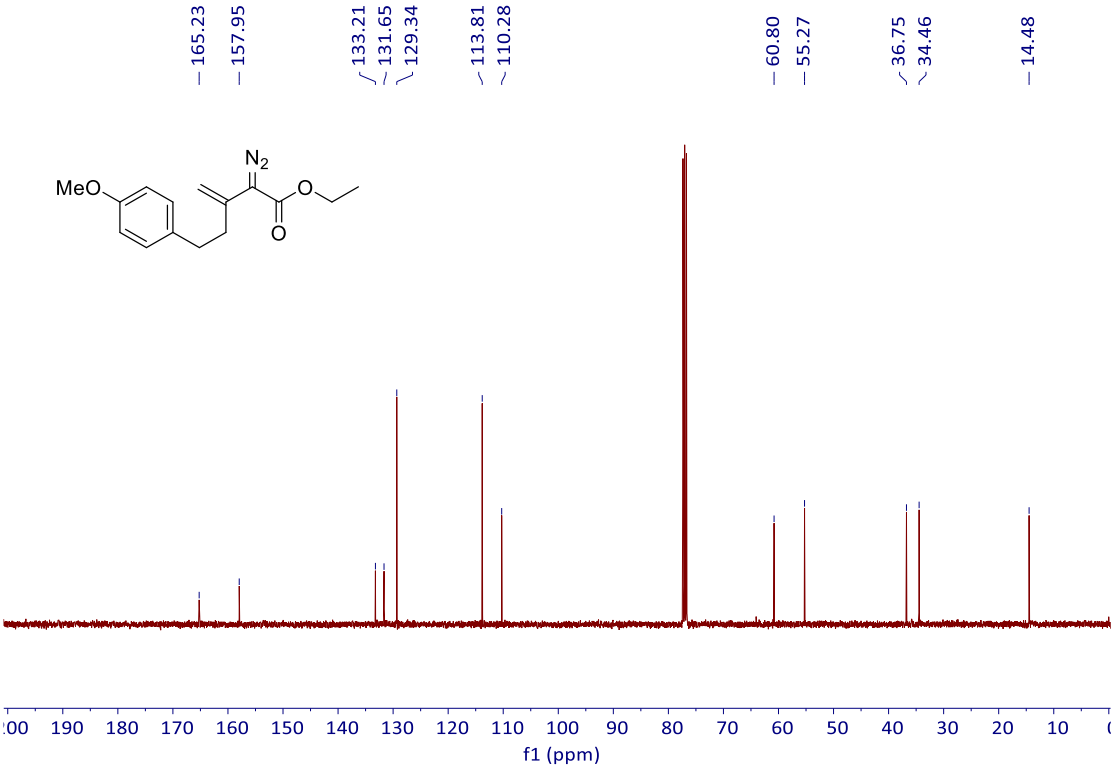

$^{1}$H NMR of **1t** (400 Hz, $CDCl_3$)



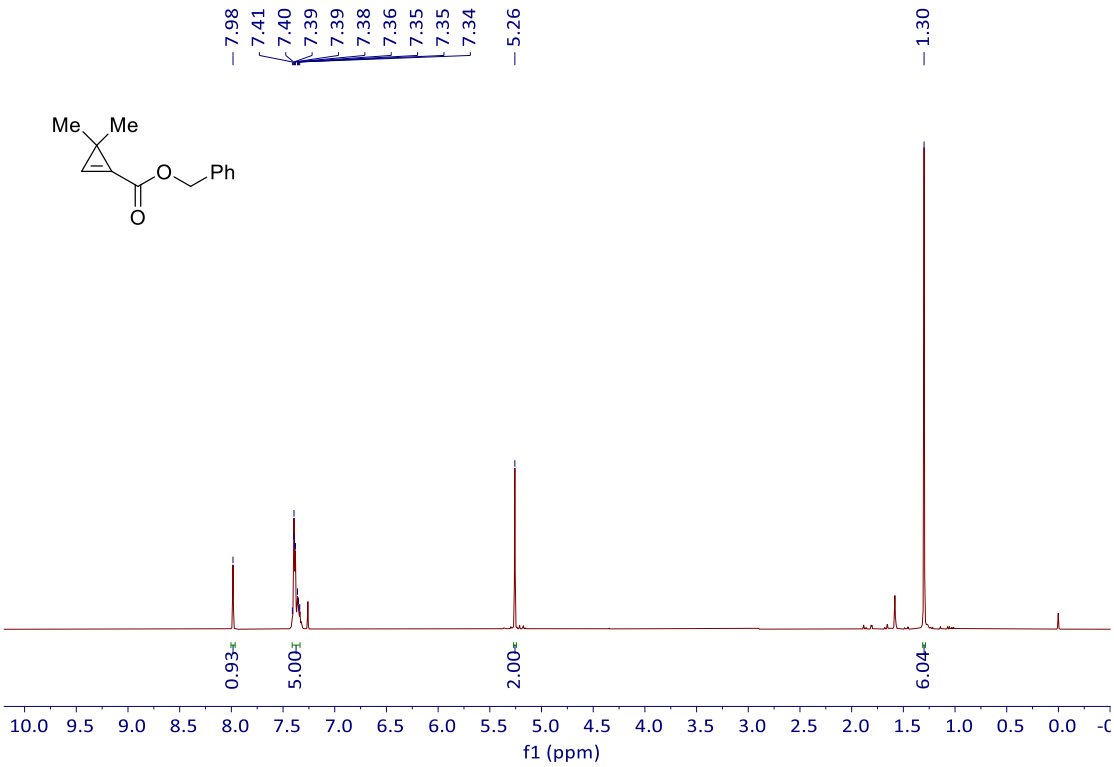

$^{13}$C NMR of **1t** (100 Hz, $CDCl_3$)



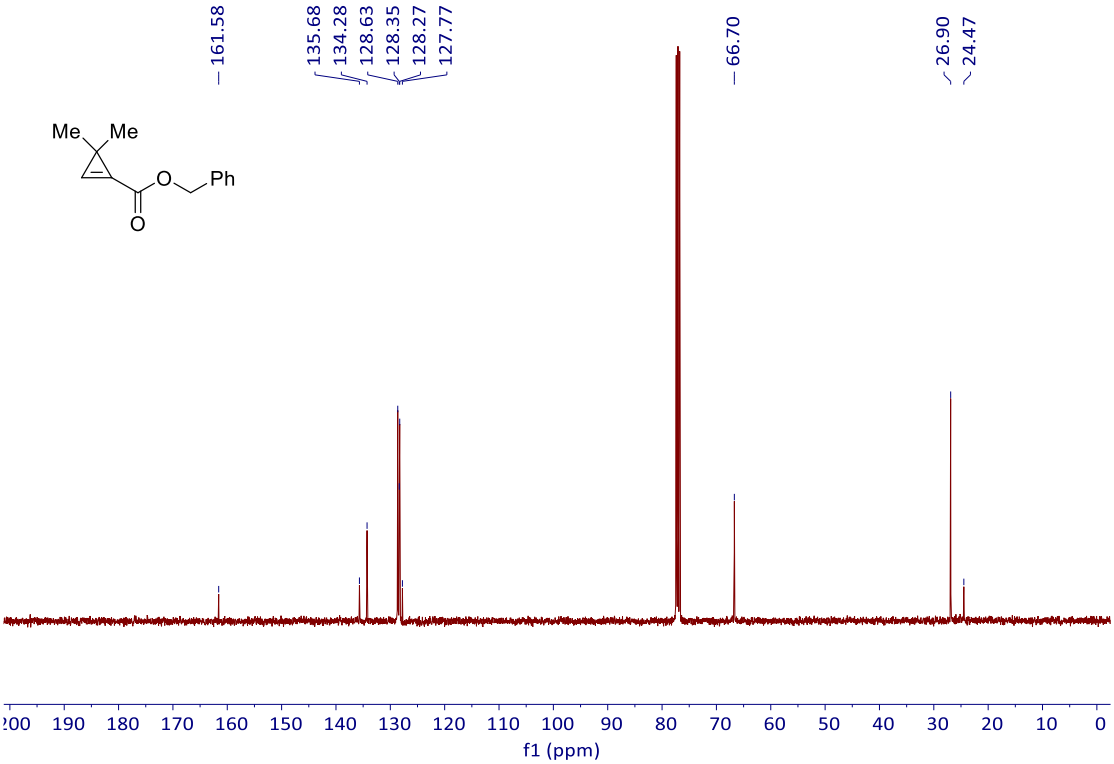

$^{1}$H NMR of **1u** (400 Hz, $CDCl_3$)



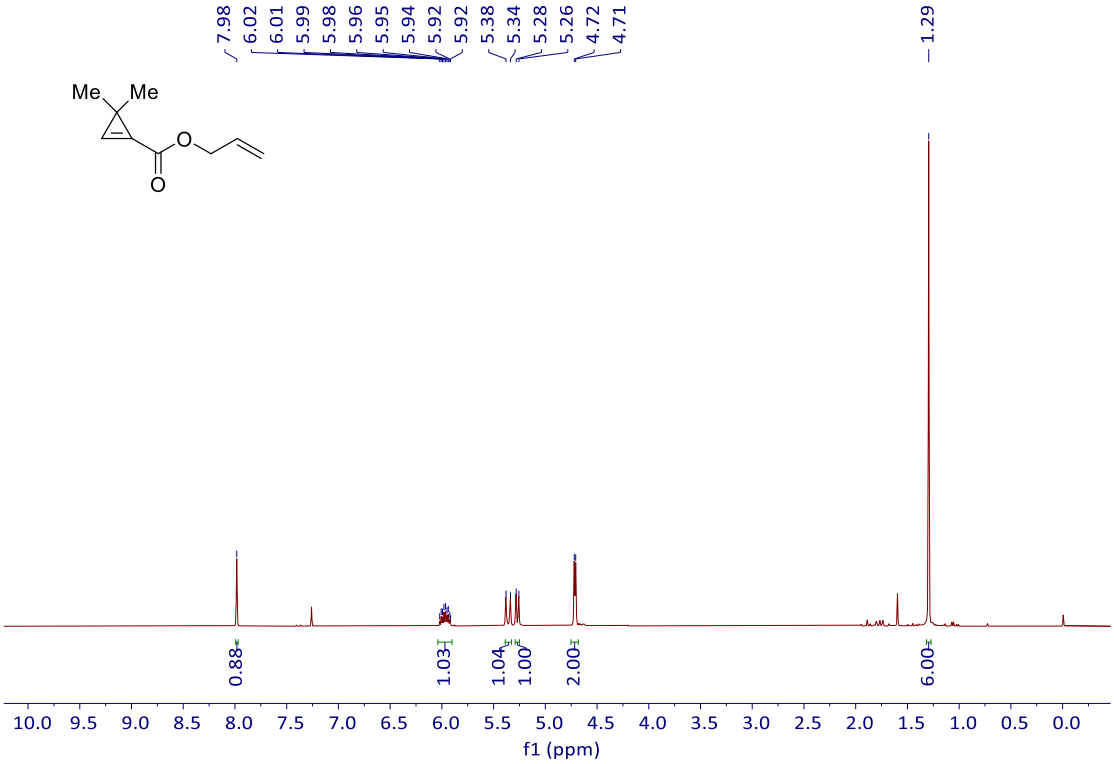

$^{13}$C NMR of **1u** (100 Hz, $CDCl_3$)



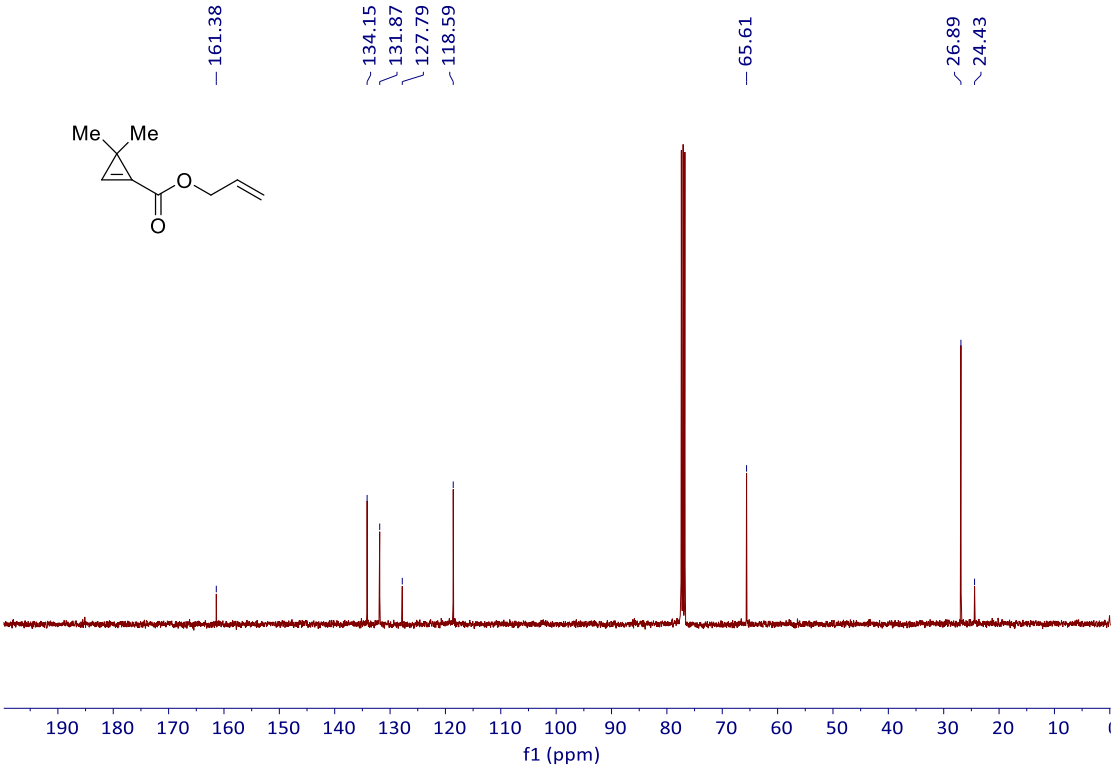

$^{1}$H NMR of **2a** (400 Hz, $CDCl_3$)



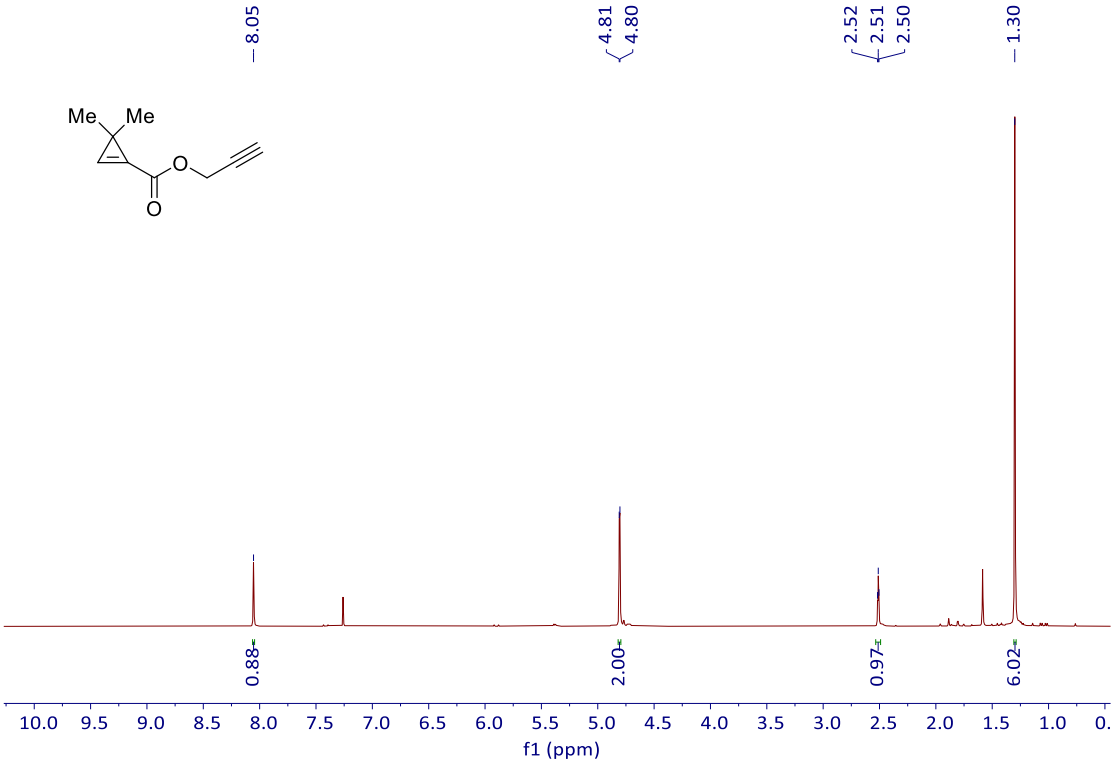

$^{13}$C NMR of **2a** (100 Hz, $CDCl_3$)



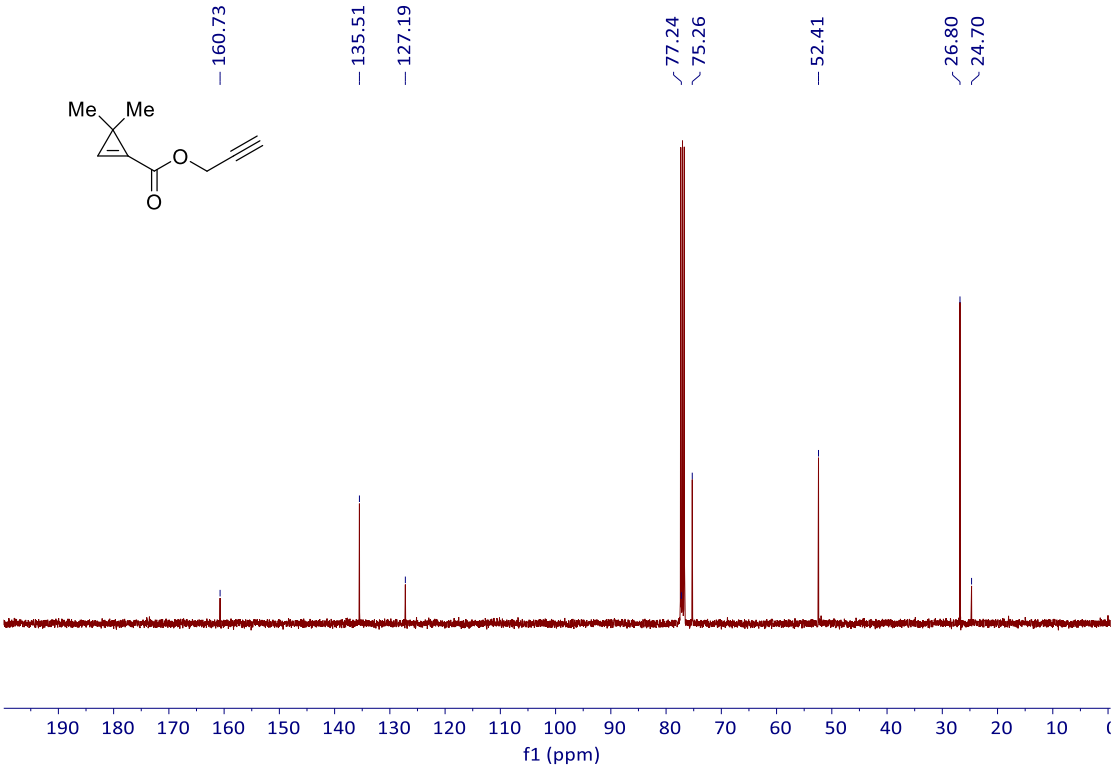

$^{1}$H NMR of **2b** (400 Hz, $CDCl_3$)



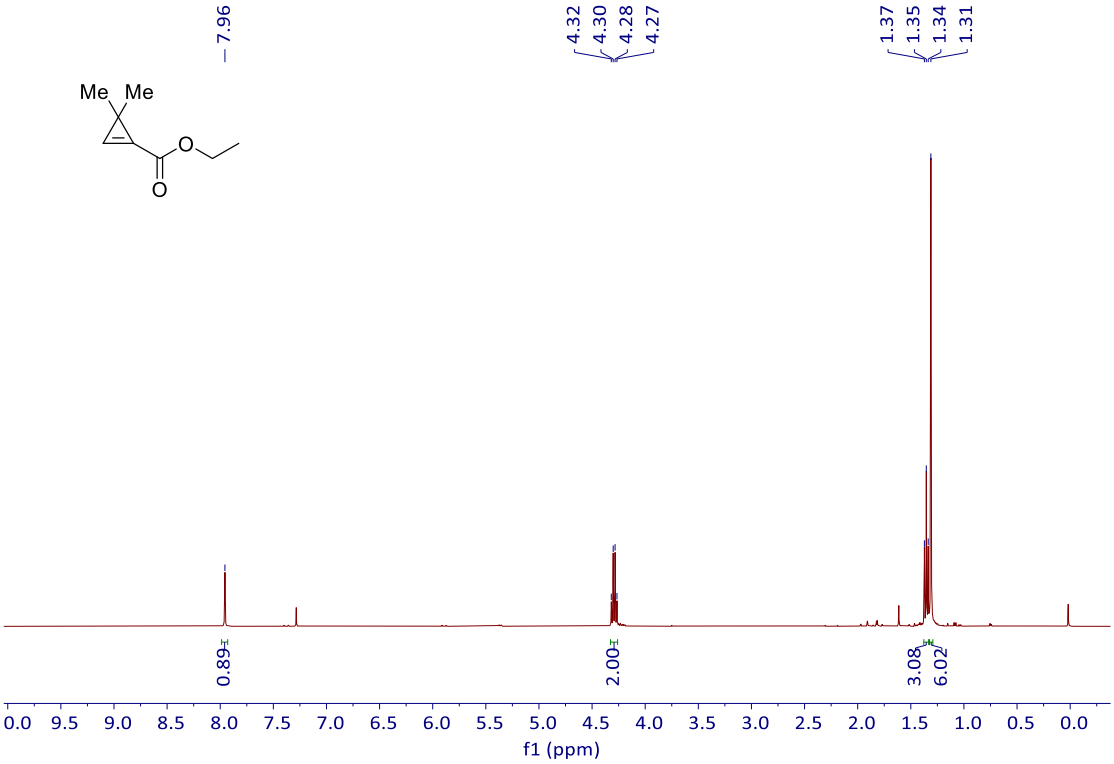

$^{13}$C NMR of **2b** (100 Hz, $CDCl_3$)



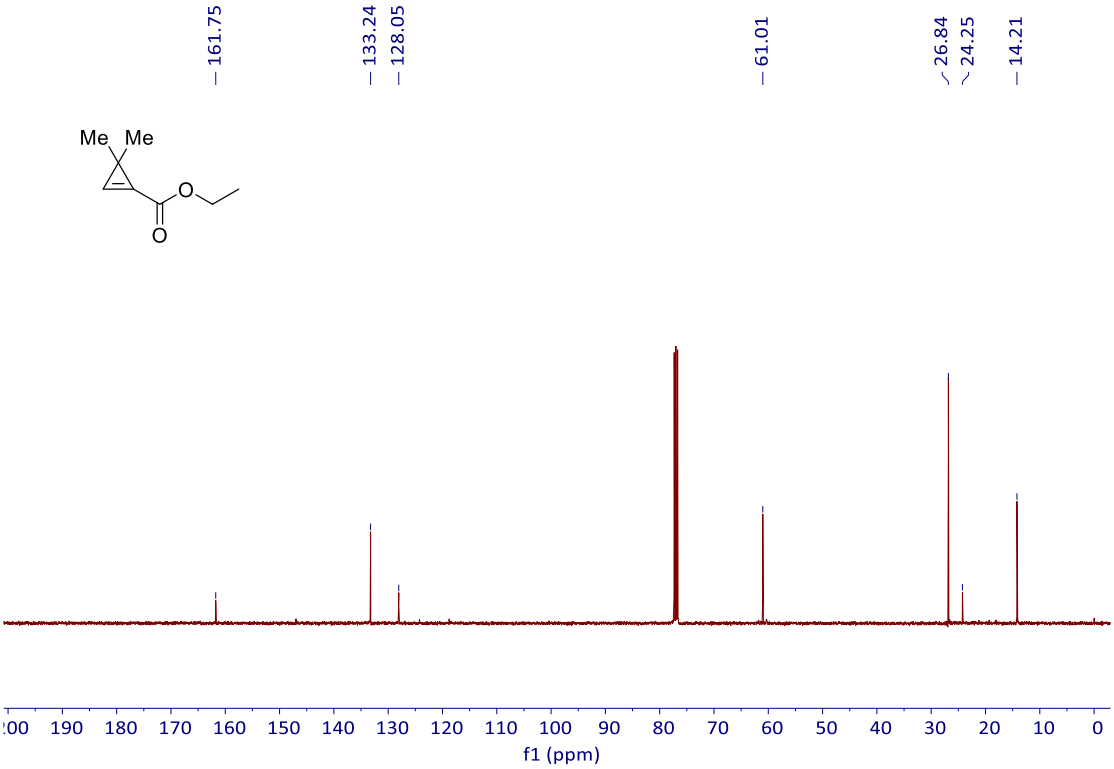

$^{1}$H NMR of **2c** (400 Hz, $CDCl_3$)



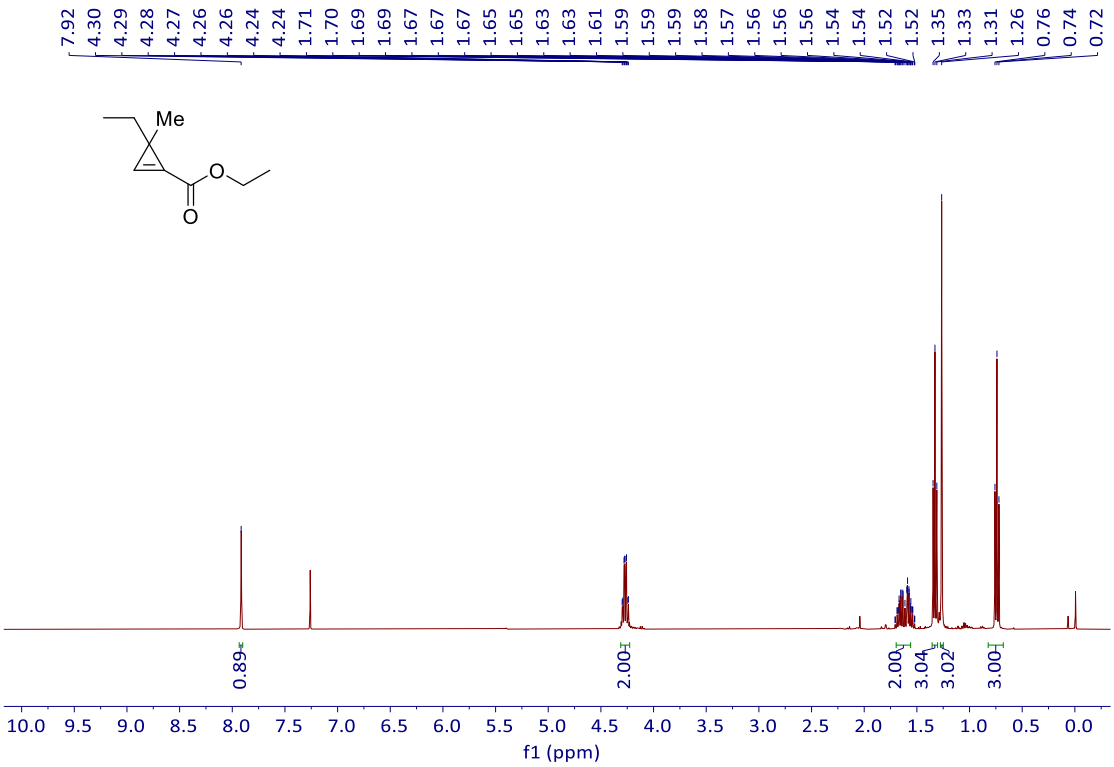

$^{13}$C NMR of **2c** (100 Hz, $CDCl_3$)



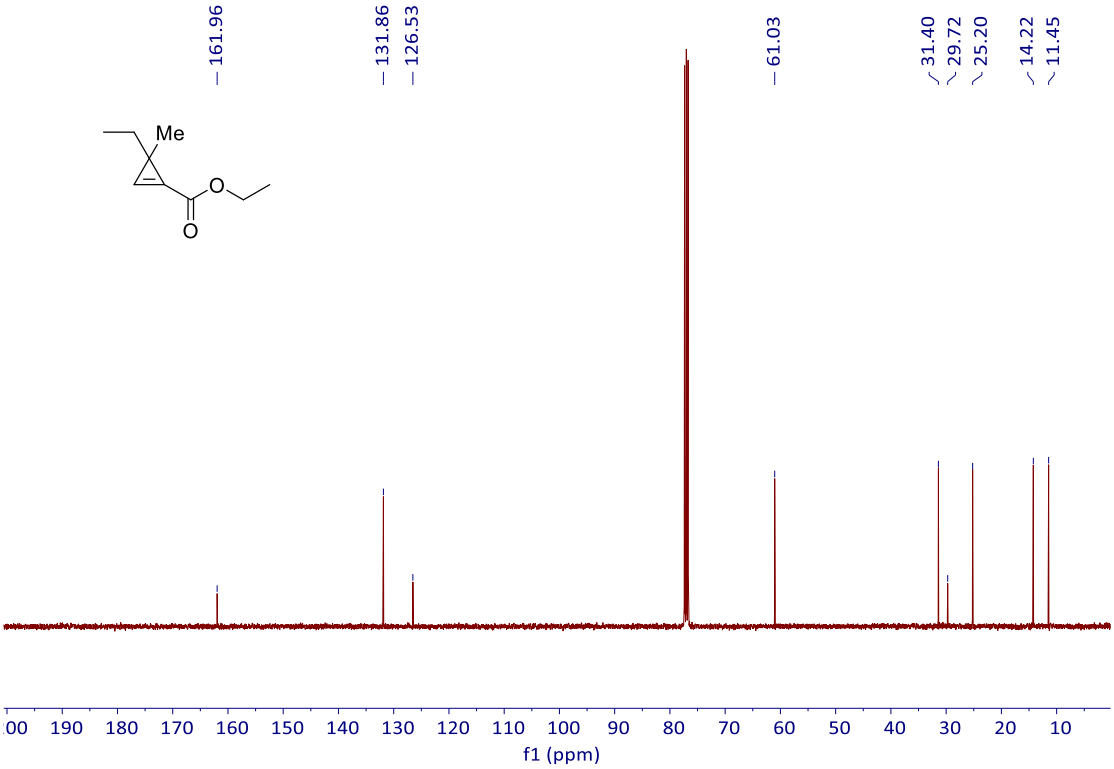

$^{1}$H NMR of **2d** (400 Hz, $CDCl_3$)



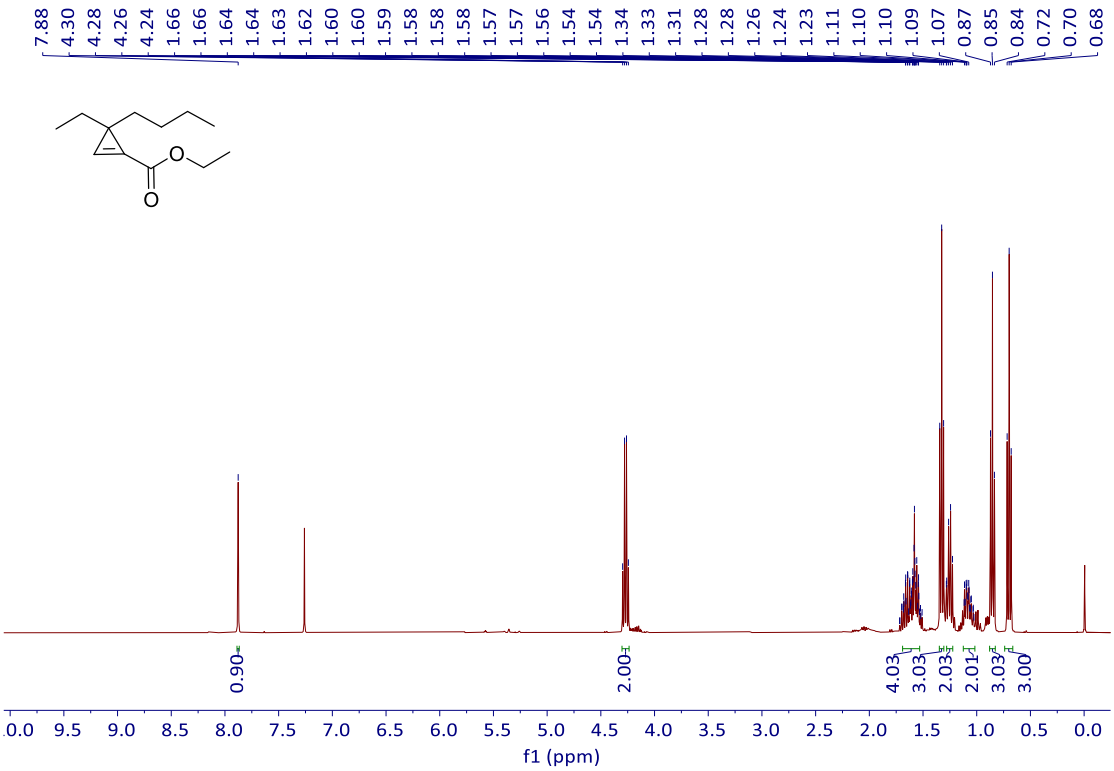

$^{13}$C NMR of **2d** (100 Hz, $CDCl_3$)



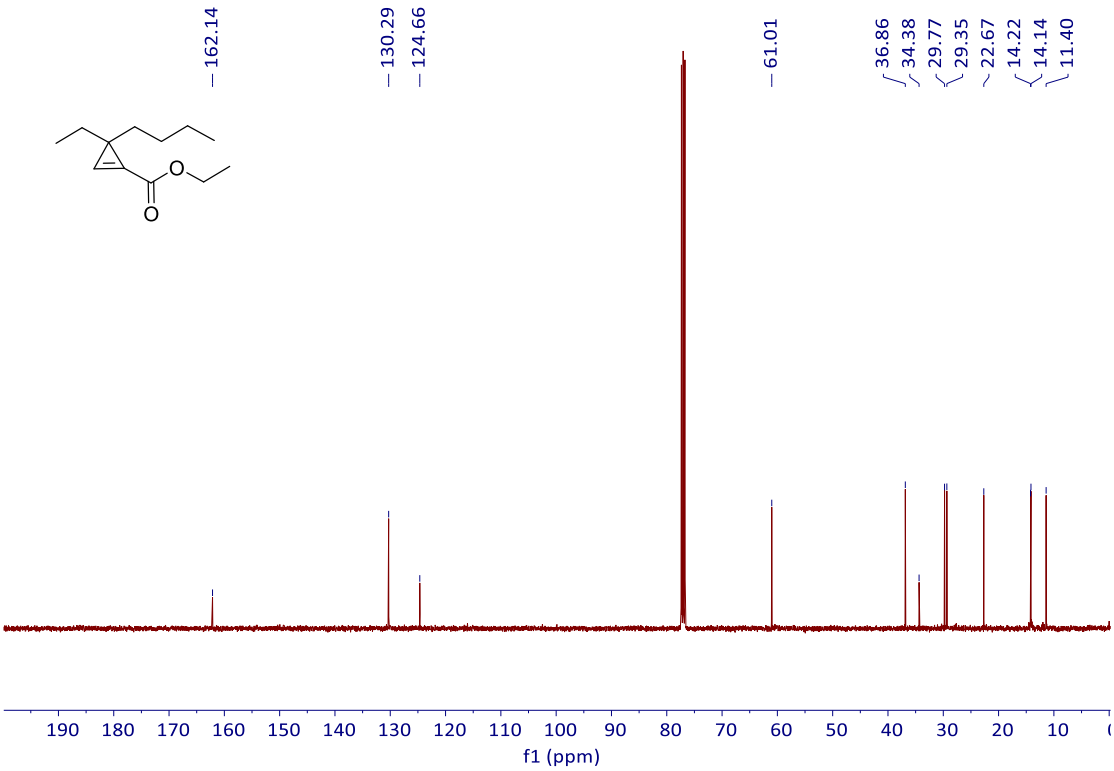

$^{1}$H NMR of **2e** (400 Hz, $CDCl_3$)



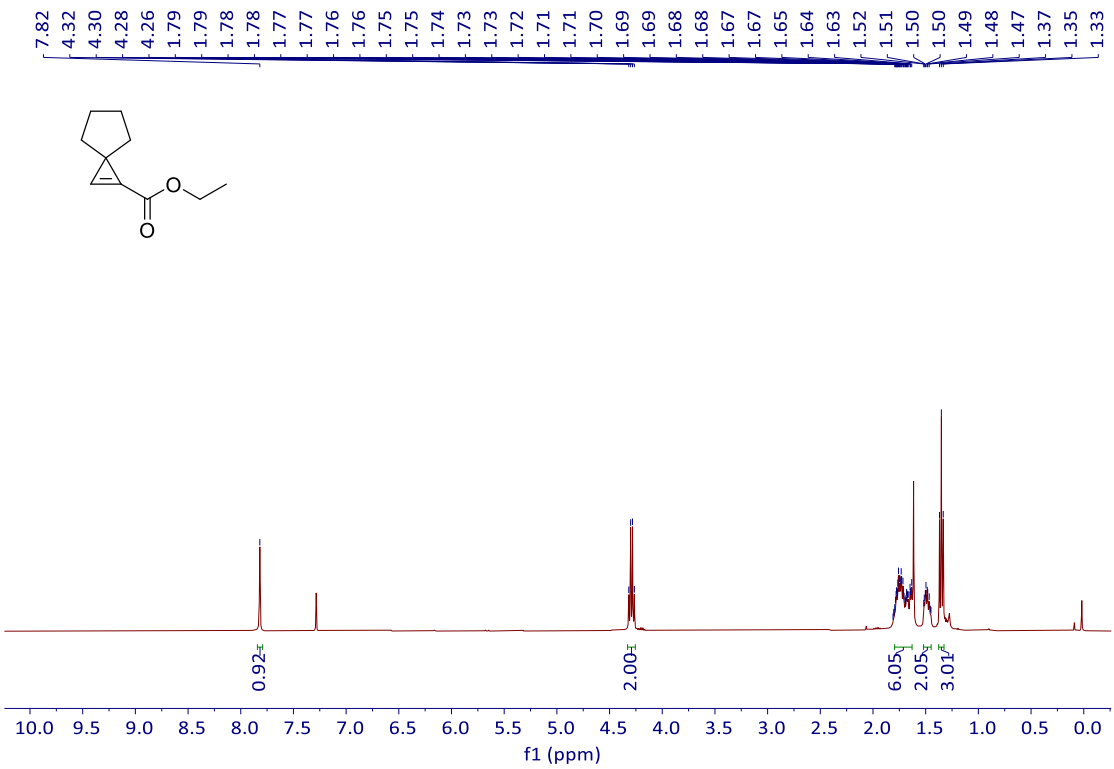

$^{13}$C NMR of **2e** (100 Hz, $CDCl_3$)



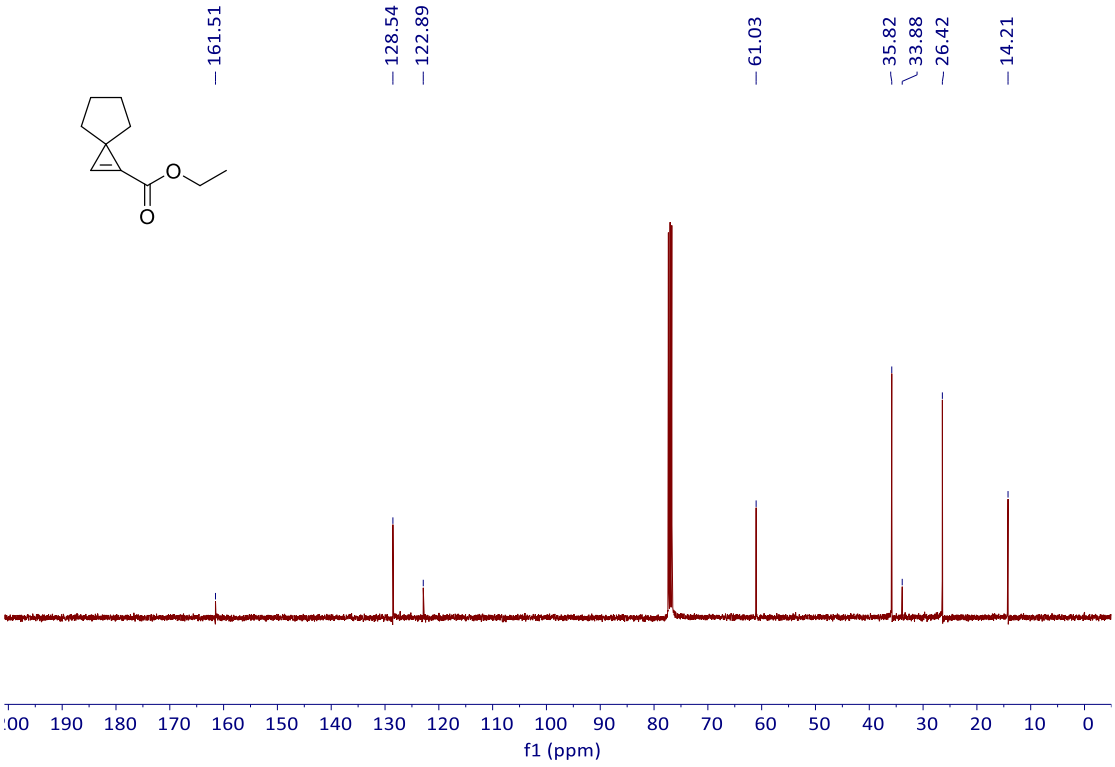

$^{1}$H NMR of **2f** (400 Hz, $CDCl_3$)



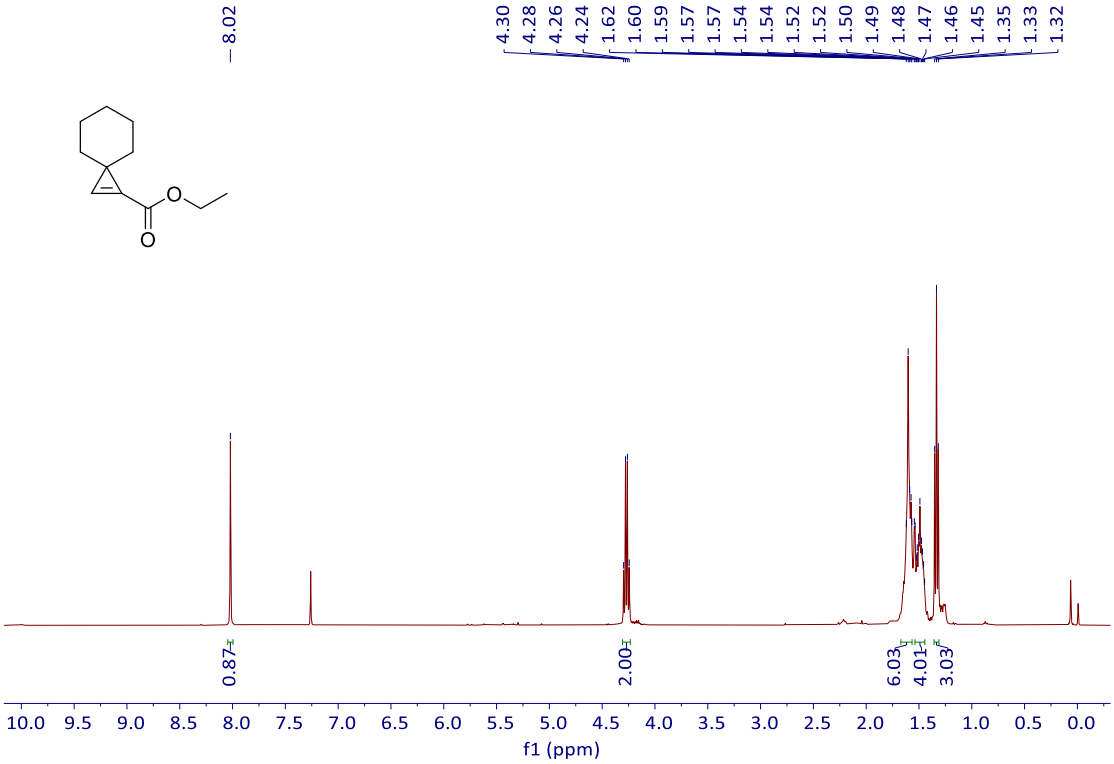

$^{13}$C NMR of **2f** (100 Hz, $CDCl_3$)



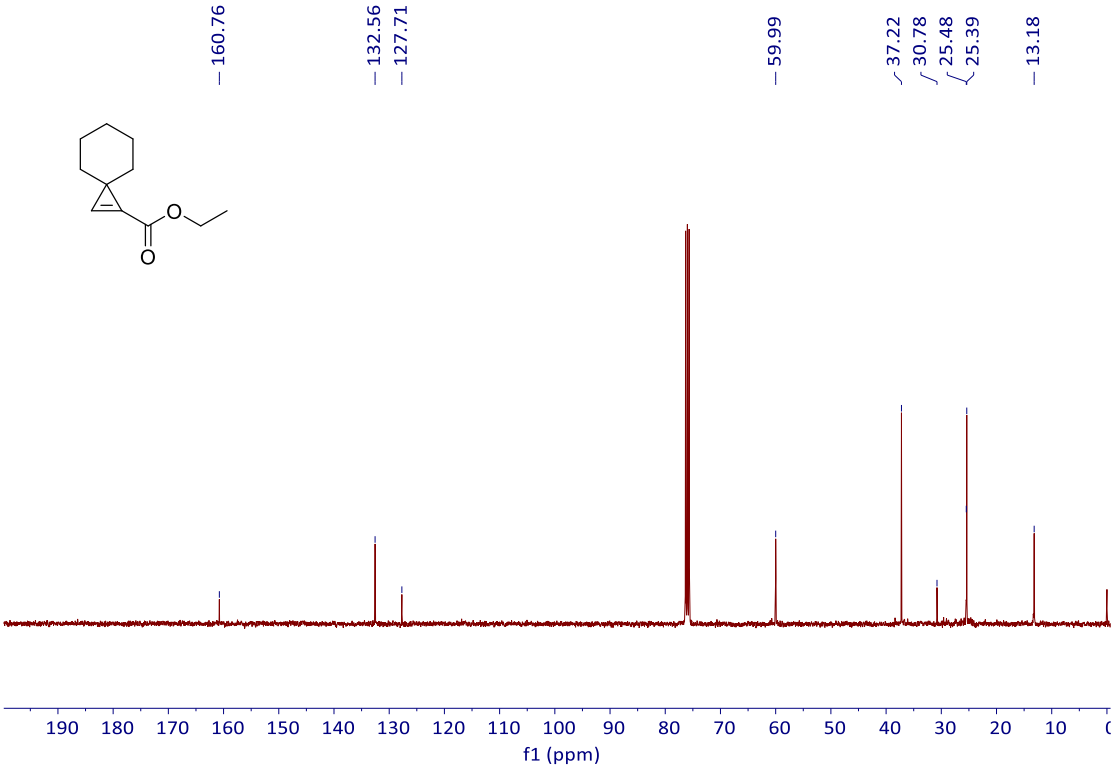

$^{1}$H NMR of **2g** (400 Hz, $CDCl_3$)



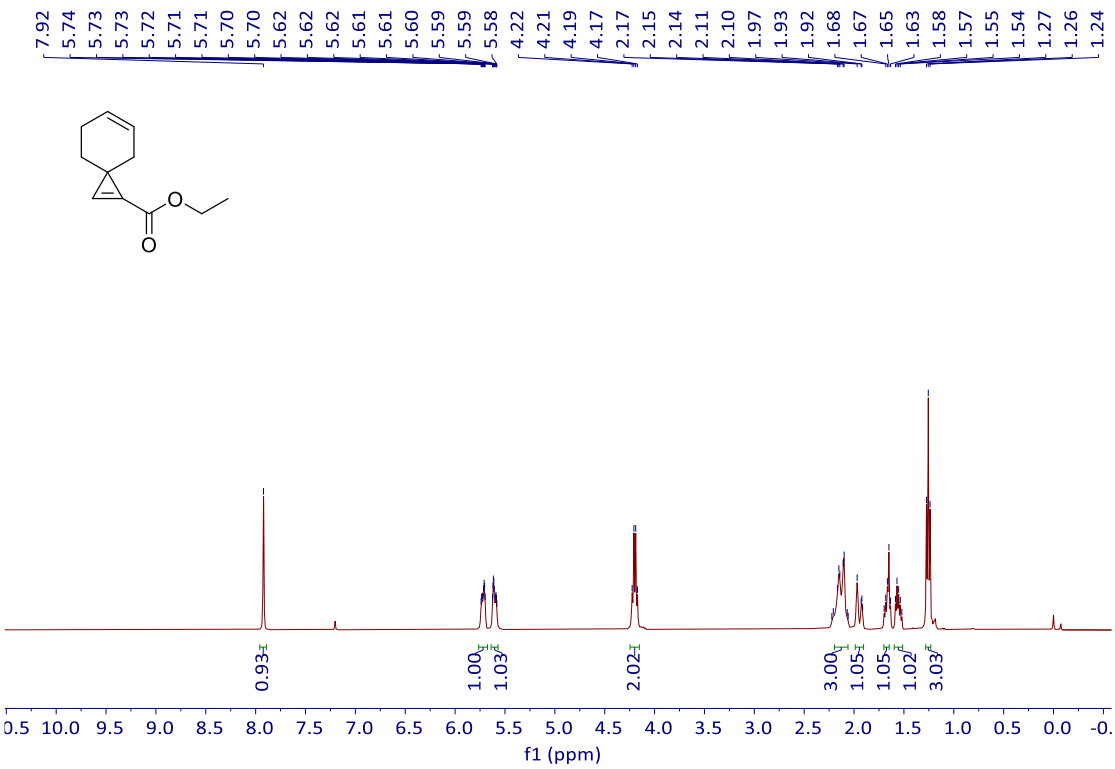

$^{13}$C NMR of **2g** (100 Hz, $CDCl_3$)



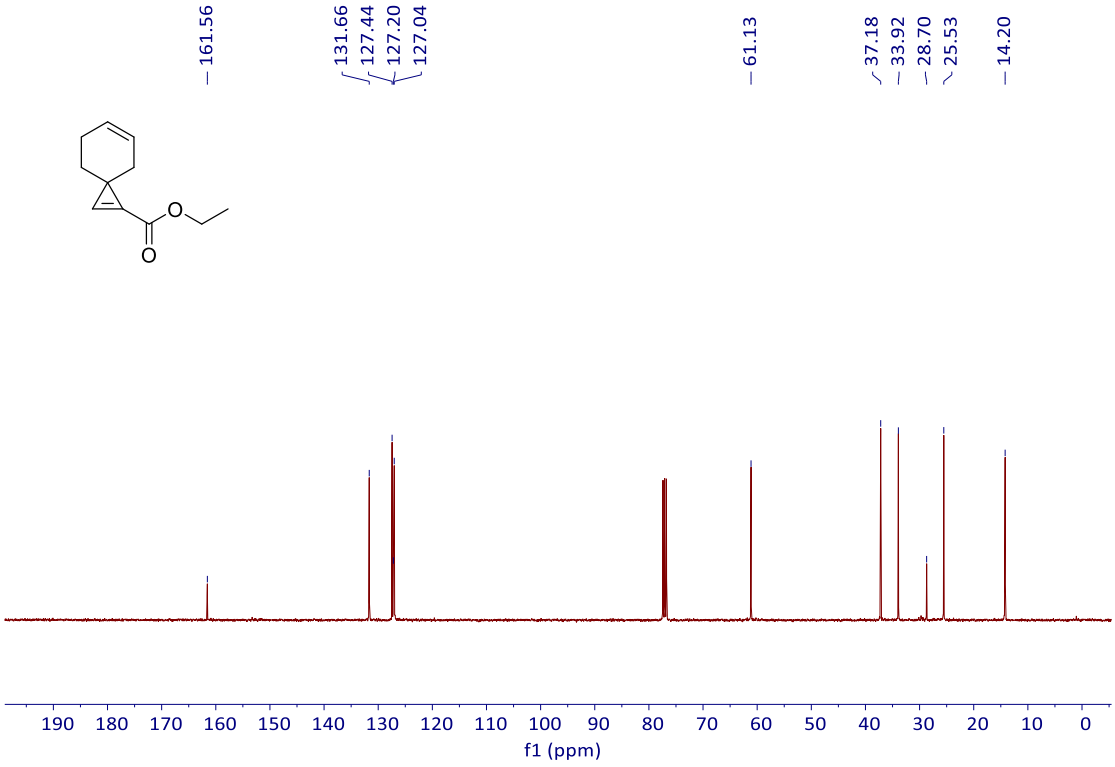

$^{1}$H NMR of **2h** (400 Hz, $CDCl_3$)



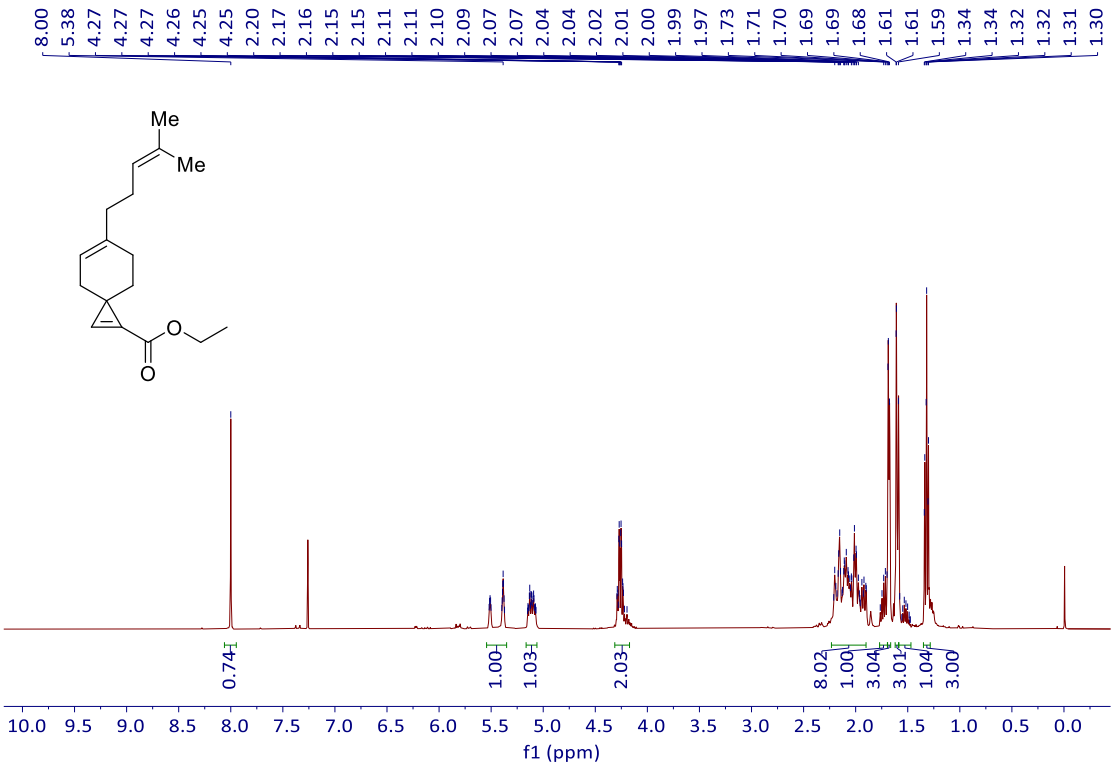

$^{13}$C NMR of **2h** (100 Hz, $CDCl_3$)



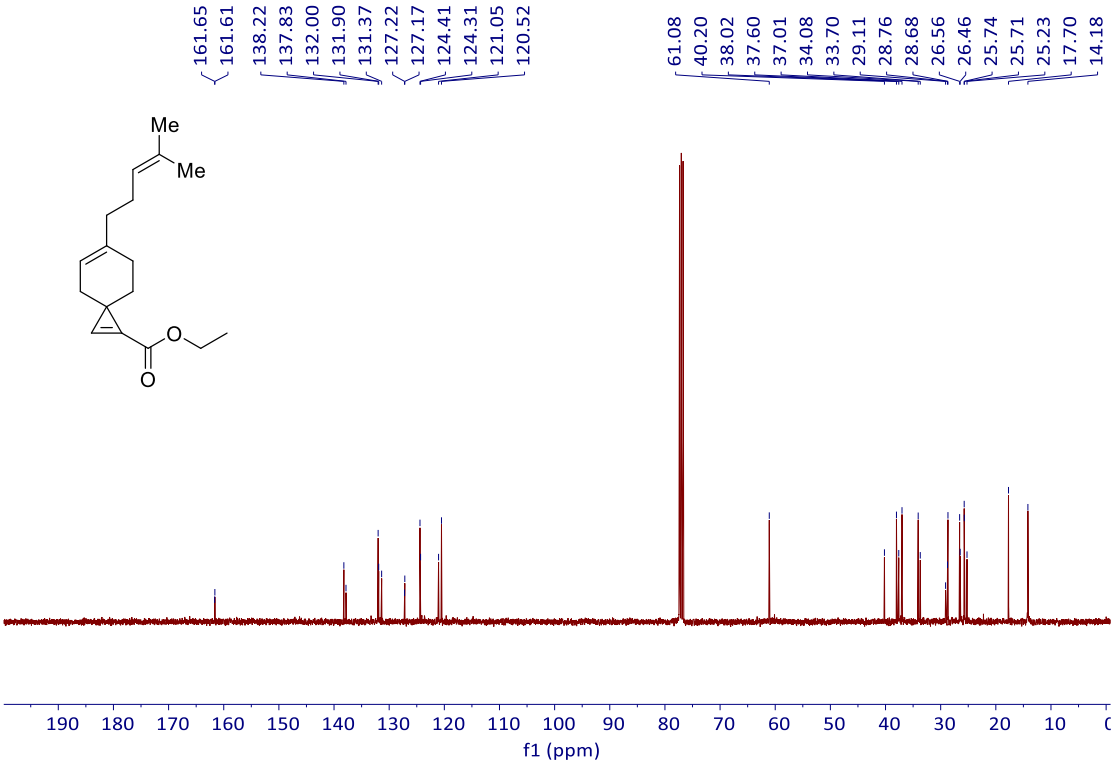

$^{1}$H NMR of **2i** (400 Hz, $CDCl_3$)



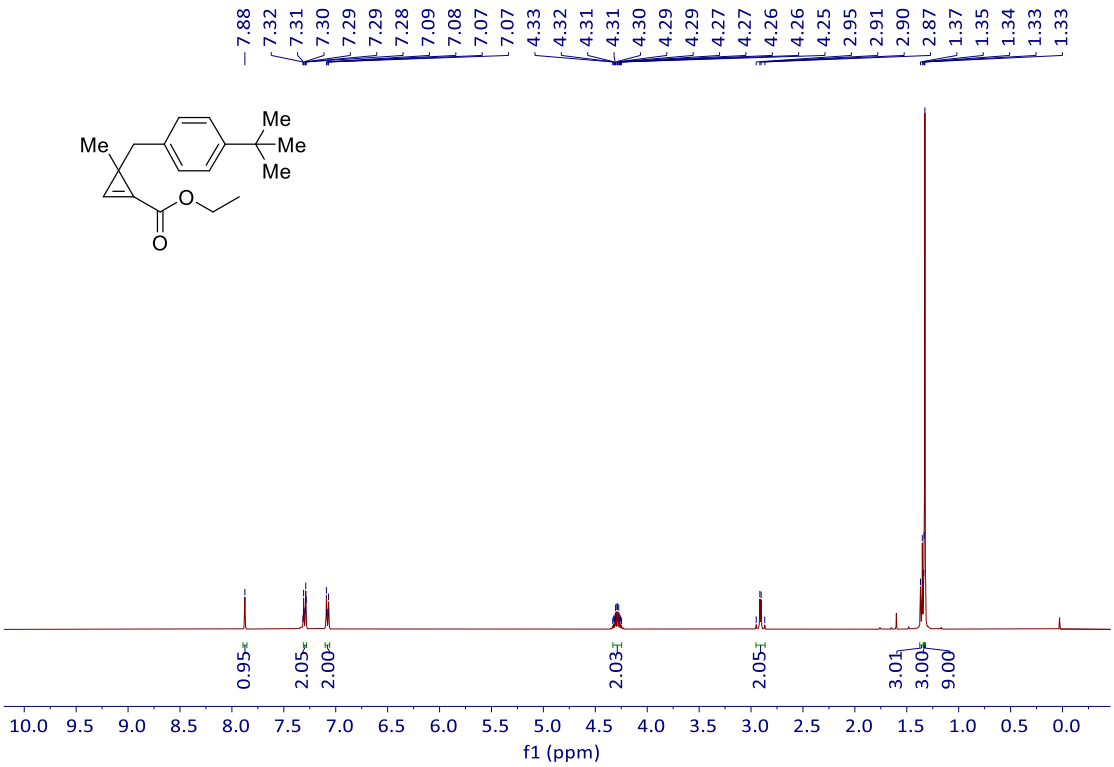

$^{13}$C NMR of **2i** (100 Hz, $CDCl_3$)



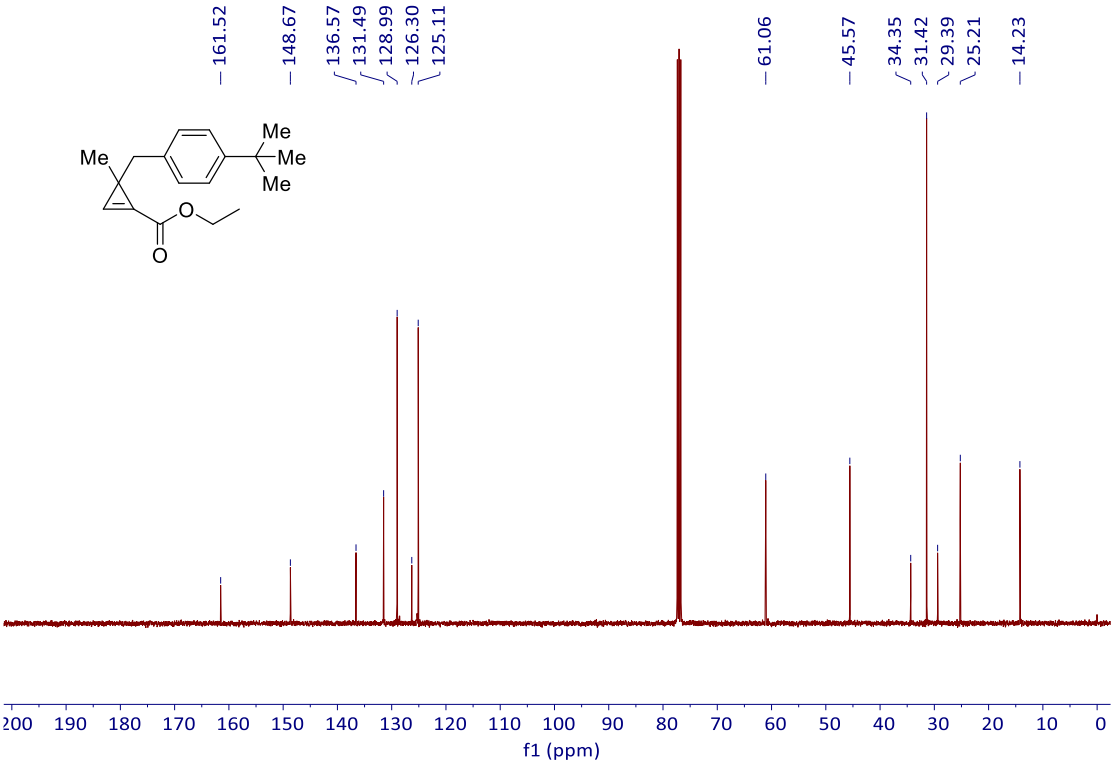

$^{1}$H NMR of **2j** (400 Hz, $CDCl_3$)



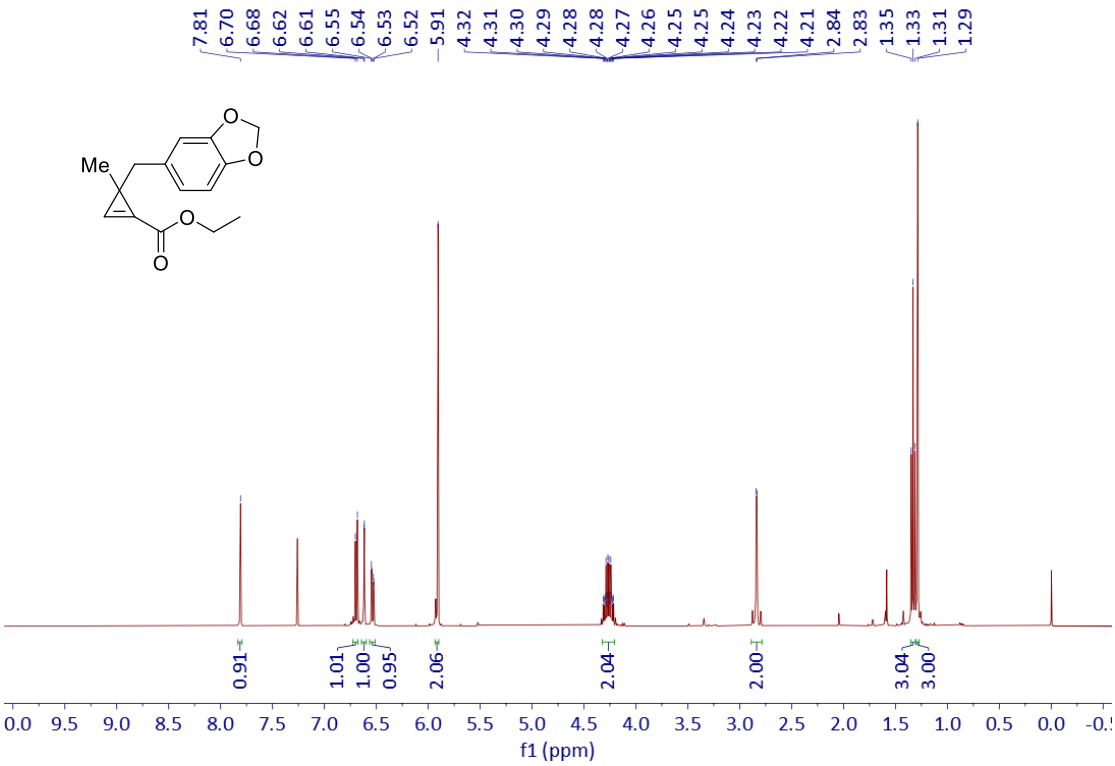

$^{13}$C NMR of **2j** (100 Hz, $CDCl_3$)



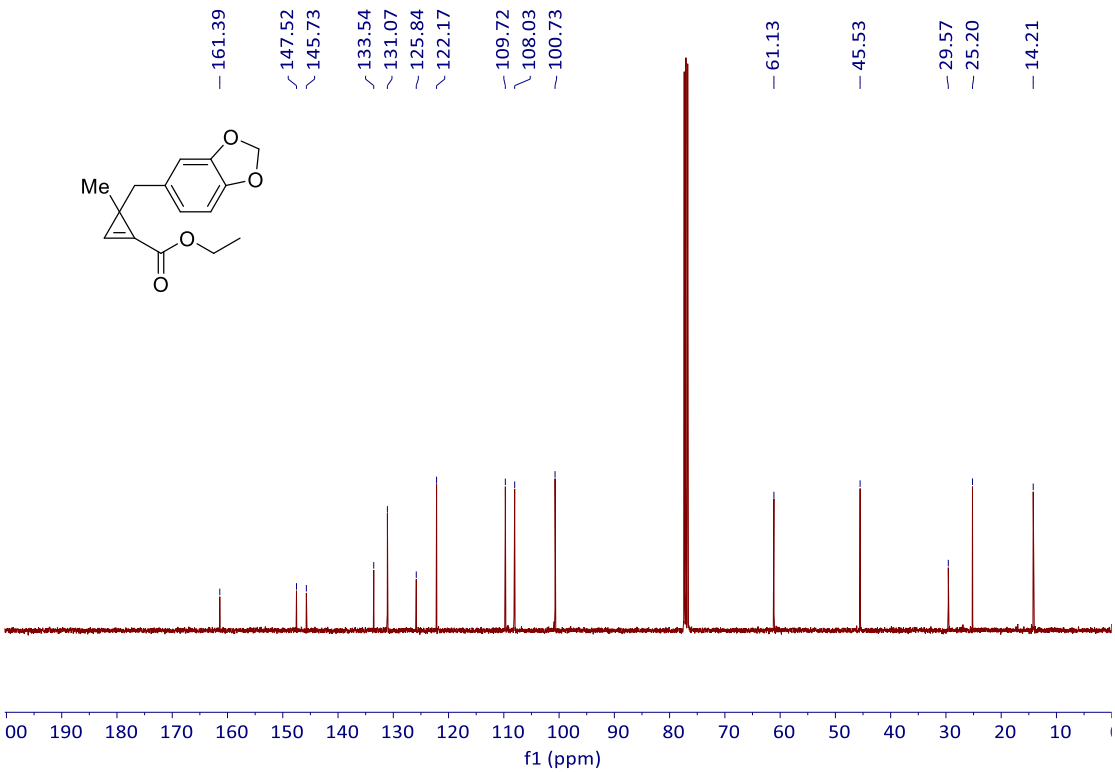

$^{1}$H NMR of **2k** (400 Hz, $CDCl_3$)



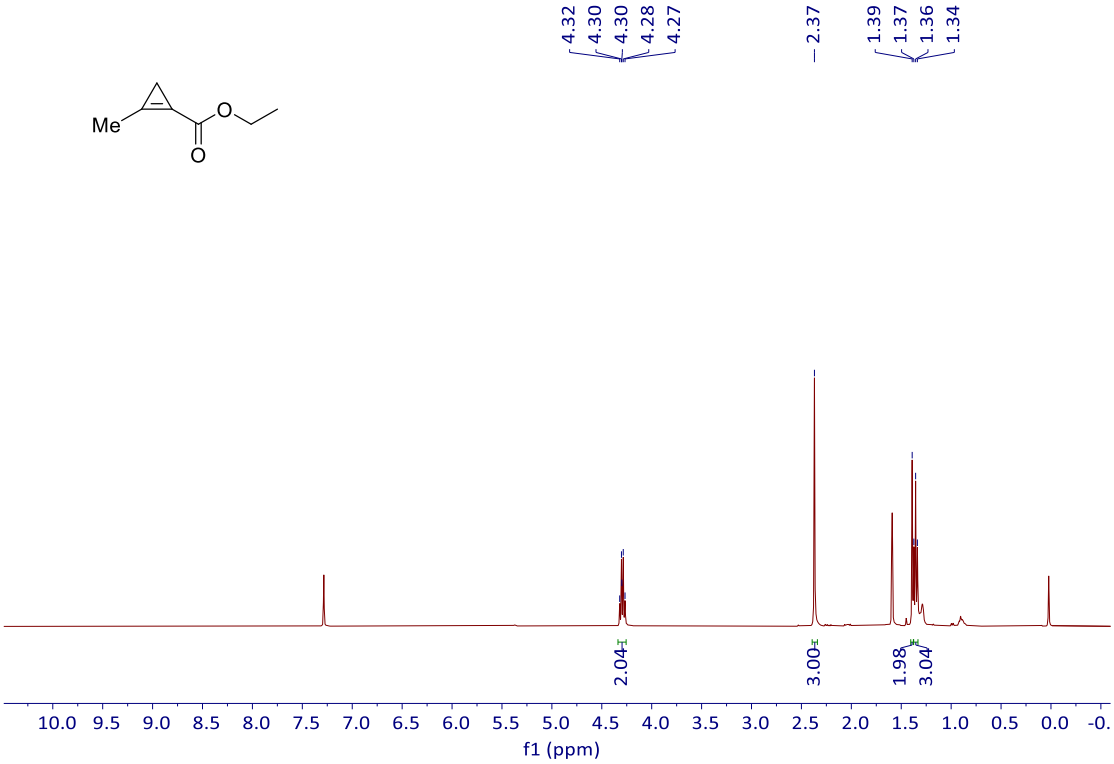

$^{13}$C NMR of **2k** (100 Hz, $CDCl_3$)



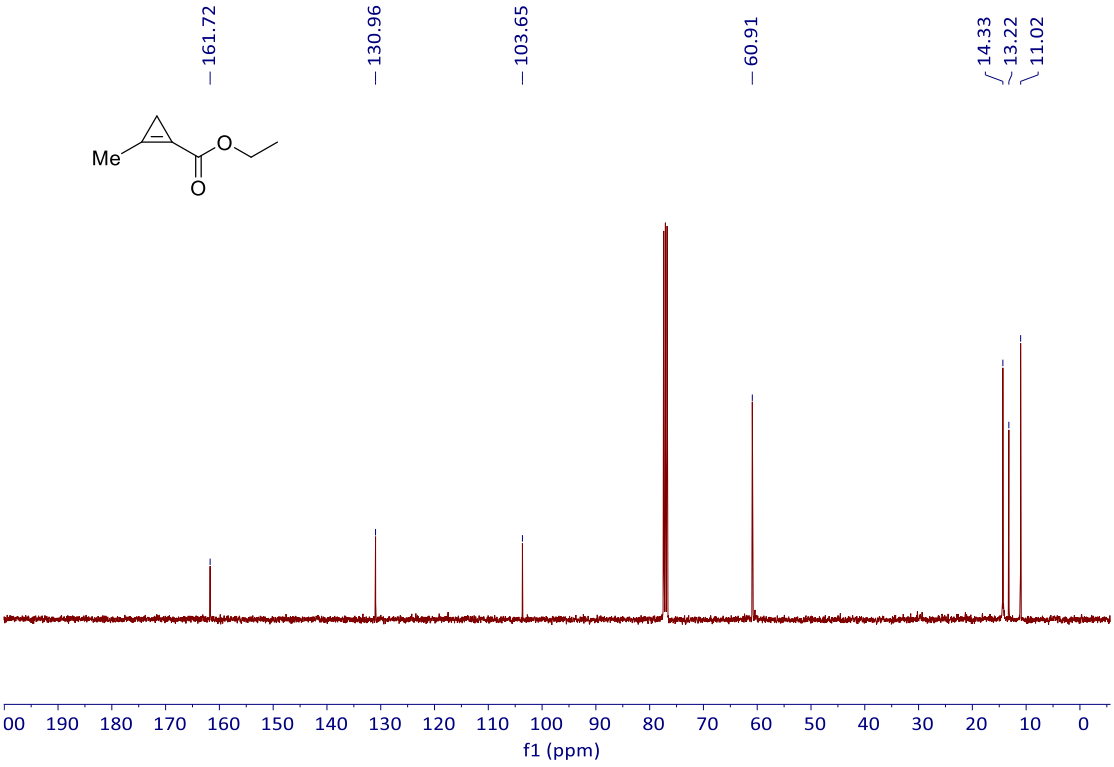

$^{1}$H NMR of **2l** (400 Hz, $CDCl_3$)



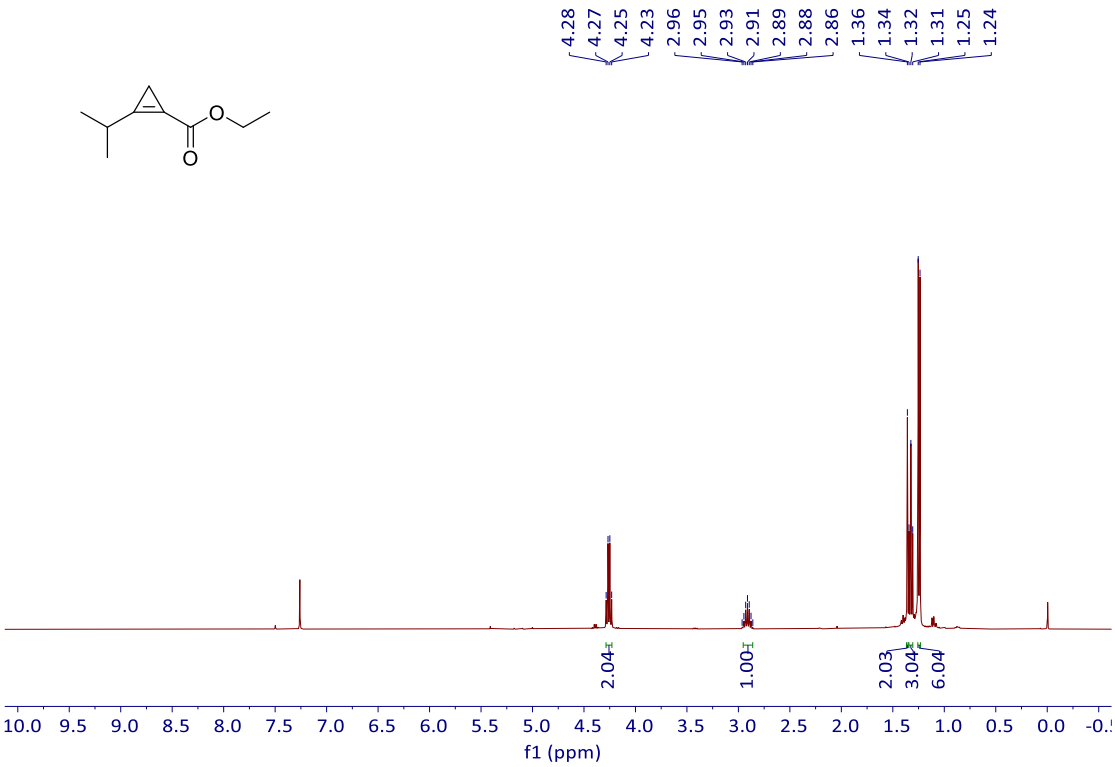

$^{13}$C NMR of **2l** (100 Hz, $CDCl_3$)



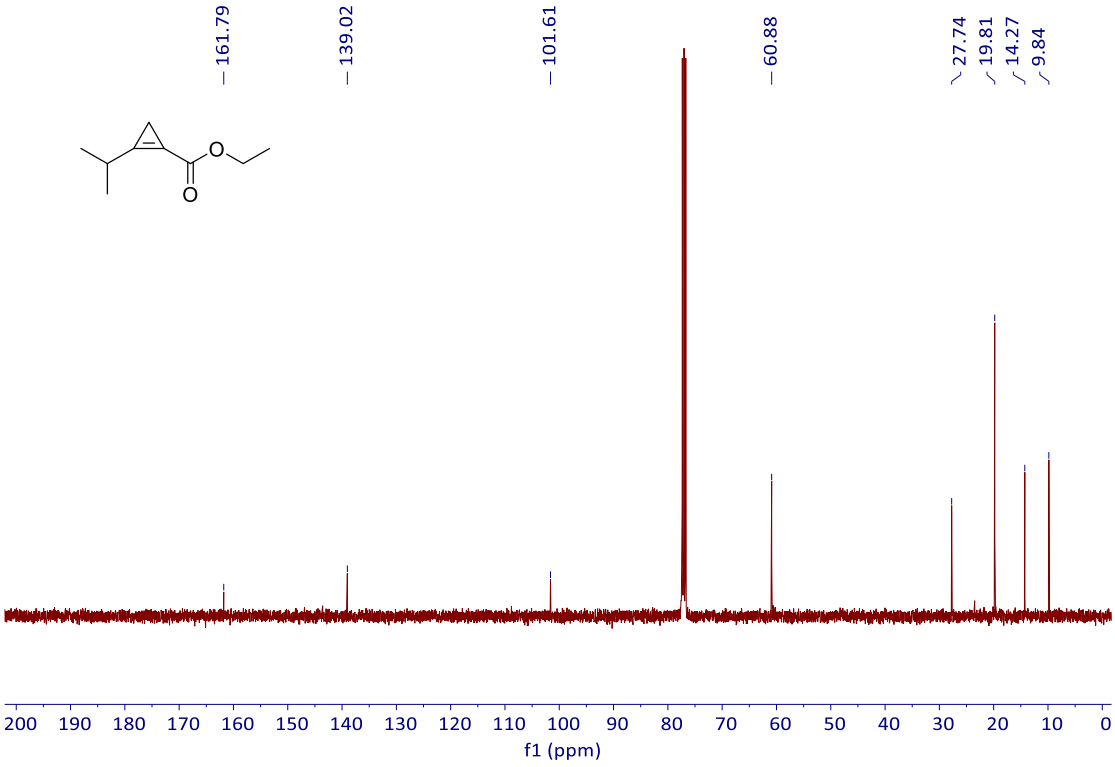

$^{1}$H NMR of **2m** (400 Hz, $CDCl_3$)



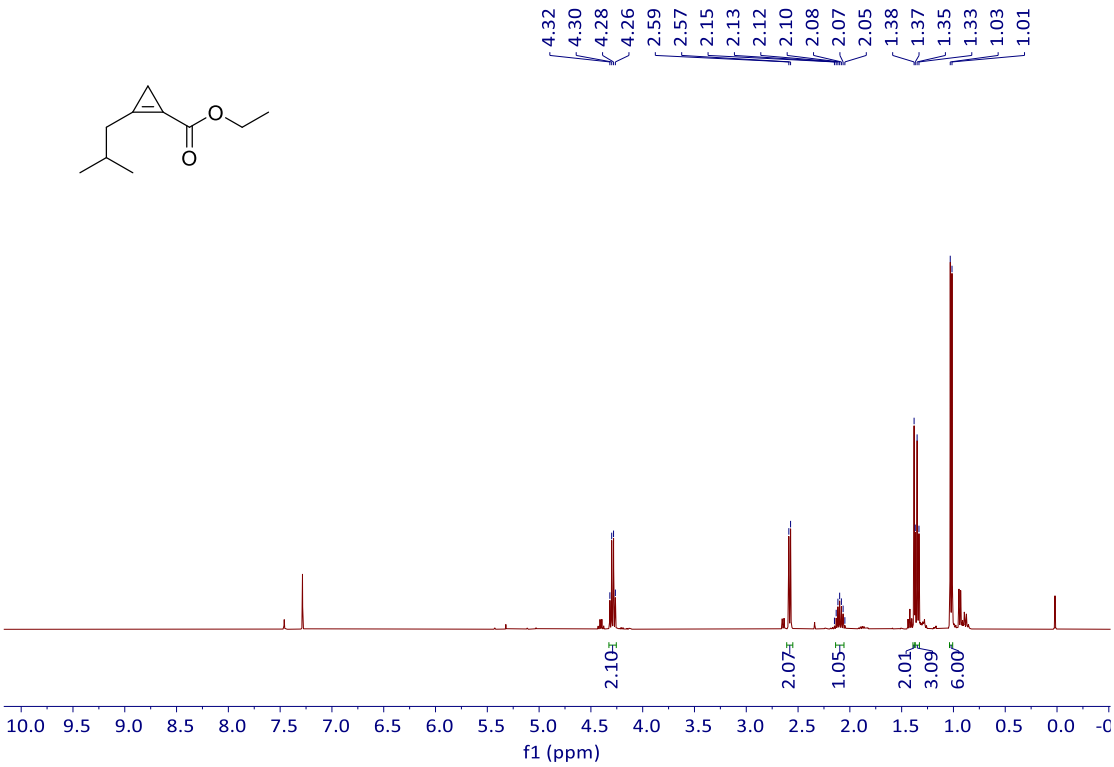

$^{13}$C NMR of **2m** (100 Hz, $CDCl_3$)



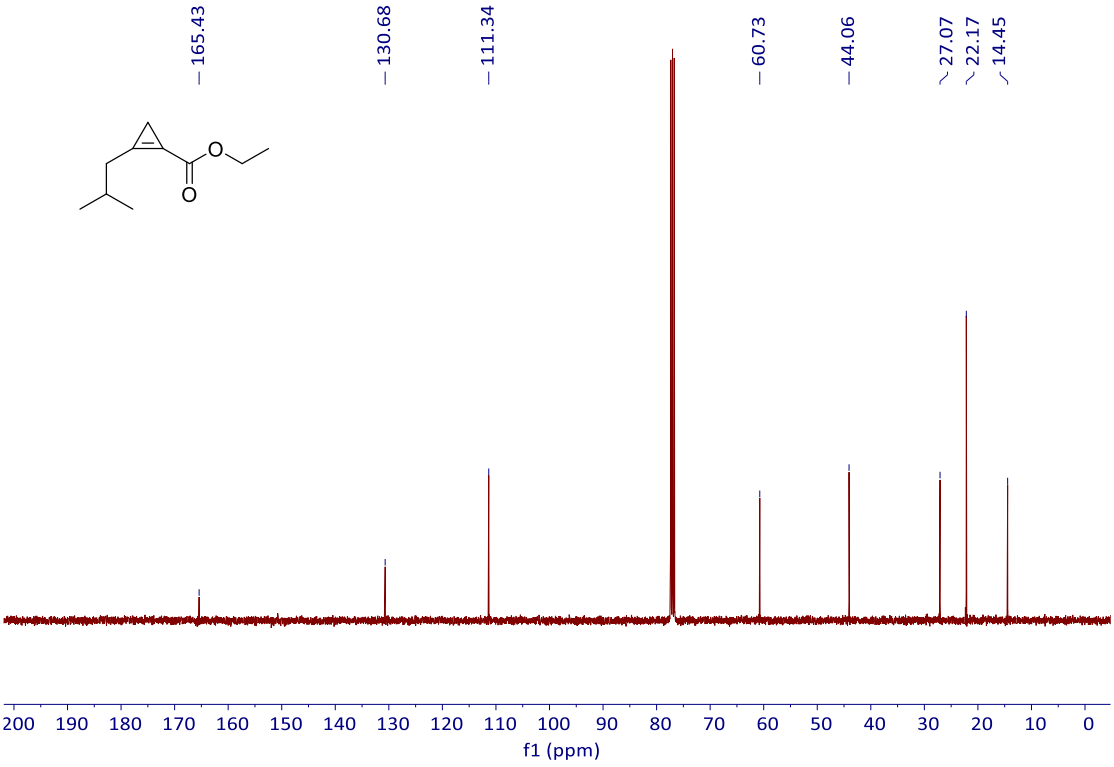

$^{1}$H NMR of **2n** (400 Hz, $CDCl_3$)



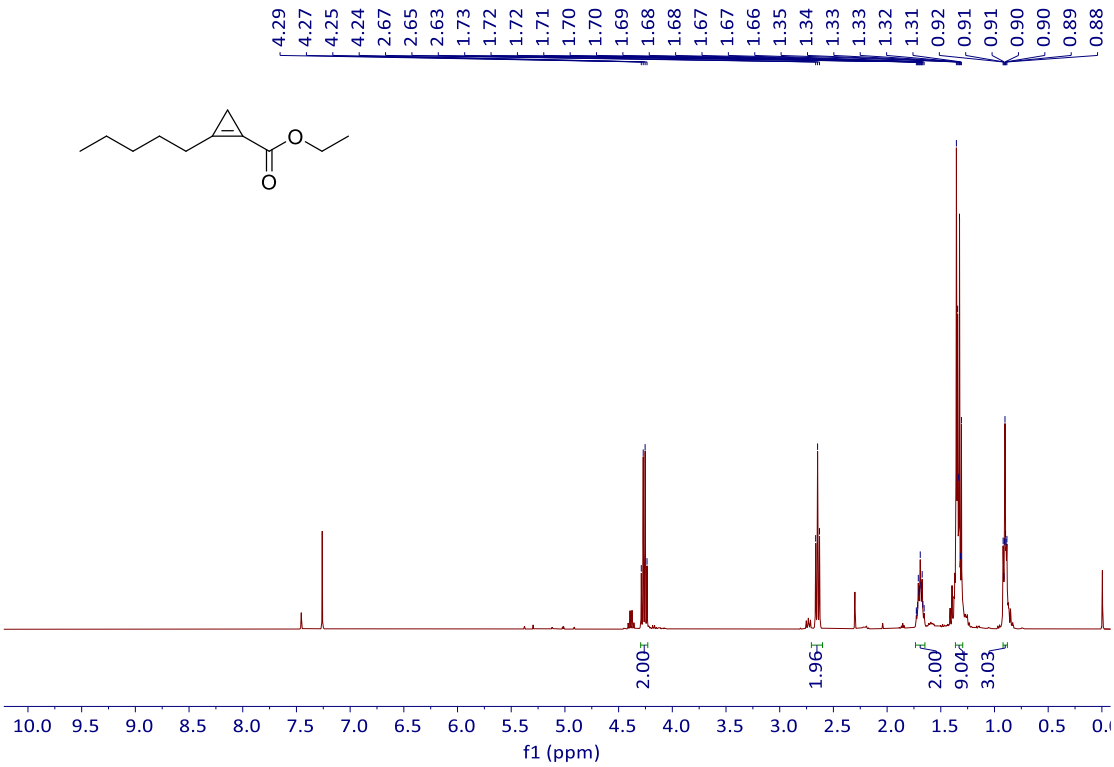

$^{13}$C NMR of **2n** (100 Hz, $CDCl_3$)



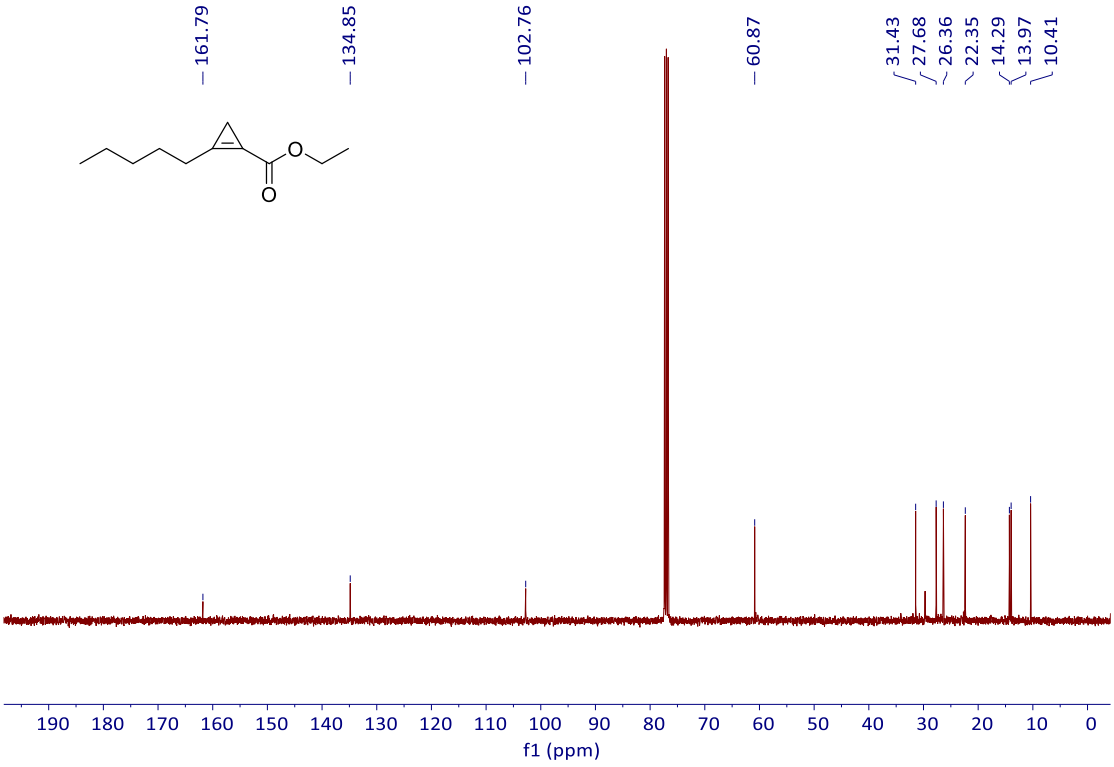

$^{1}$H NMR of **2o** (400 Hz, $CDCl_3$)



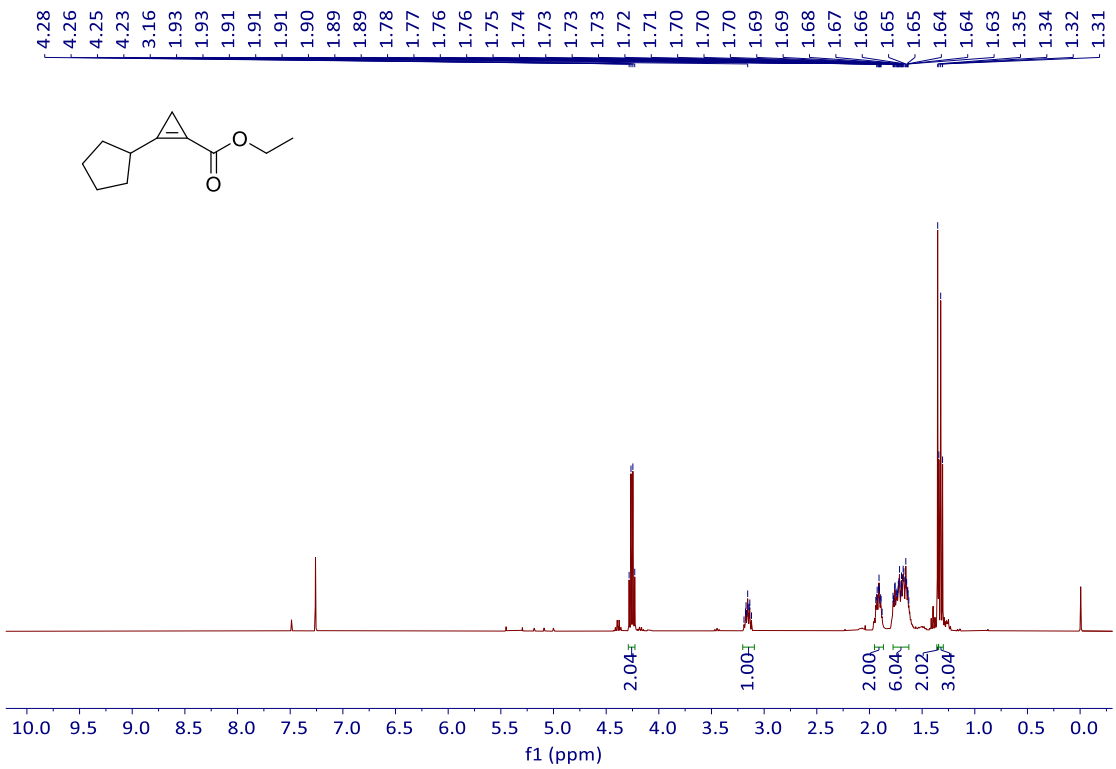

$^{13}$C NMR of **2o** (100 Hz, $CDCl_3$)



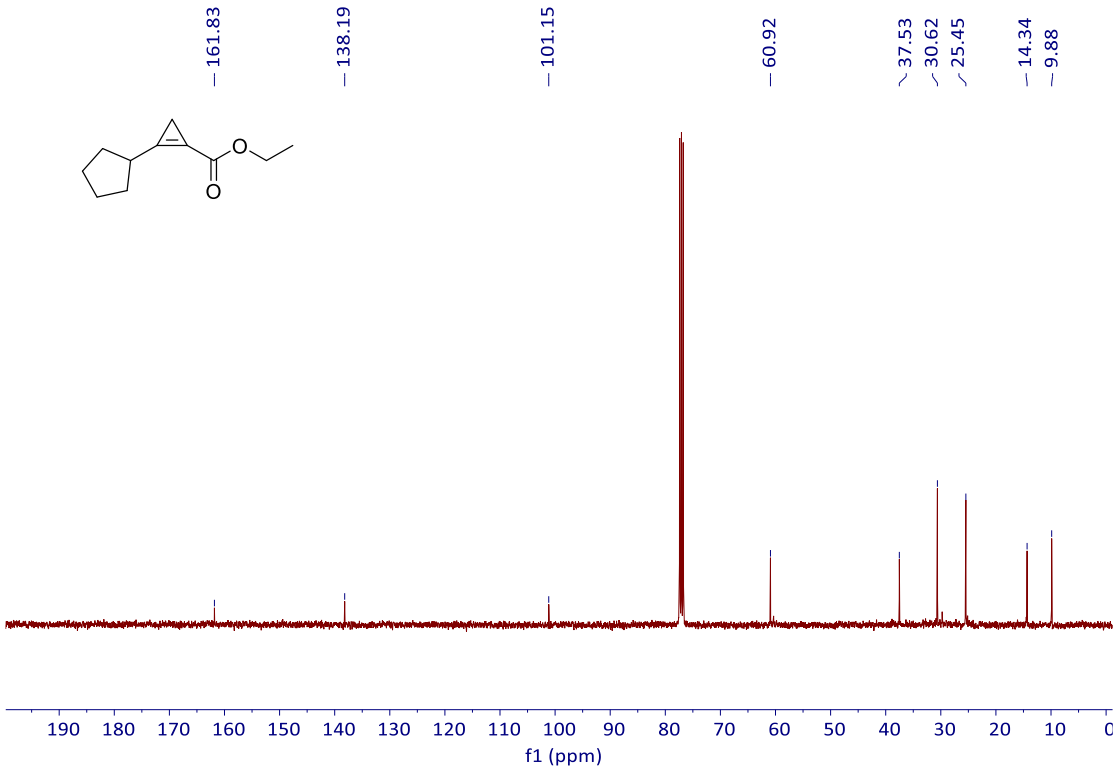

$^{1}$H NMR of **2p**(400 Hz, $CDCl_3$)



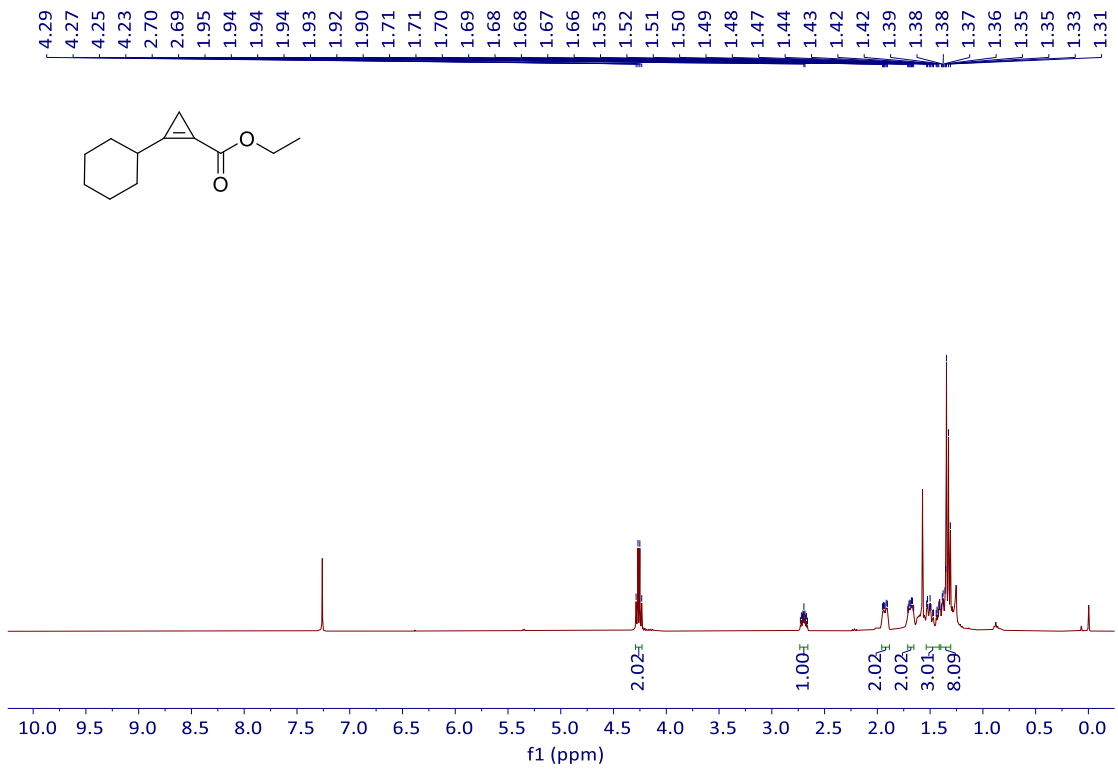

$^{13}$C NMR of **2p** (100 Hz, $CDCl_3$)



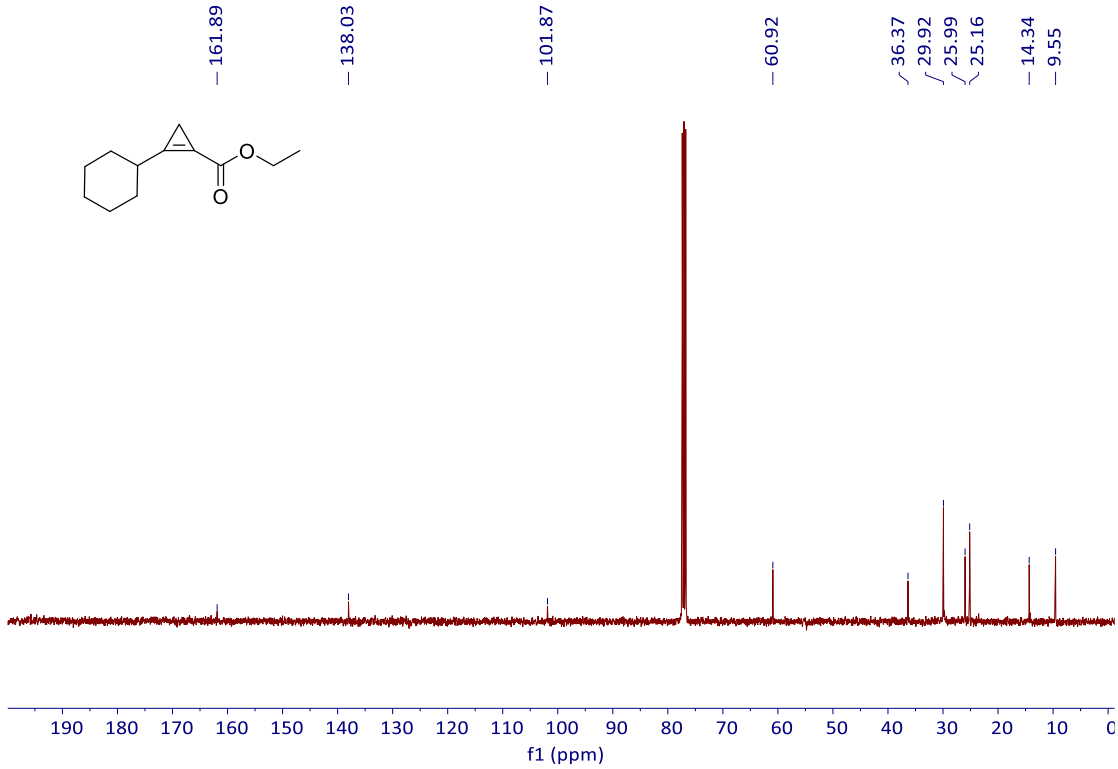

$^{1}$H NMR of **2q** (400 Hz, $CDCl_3$)



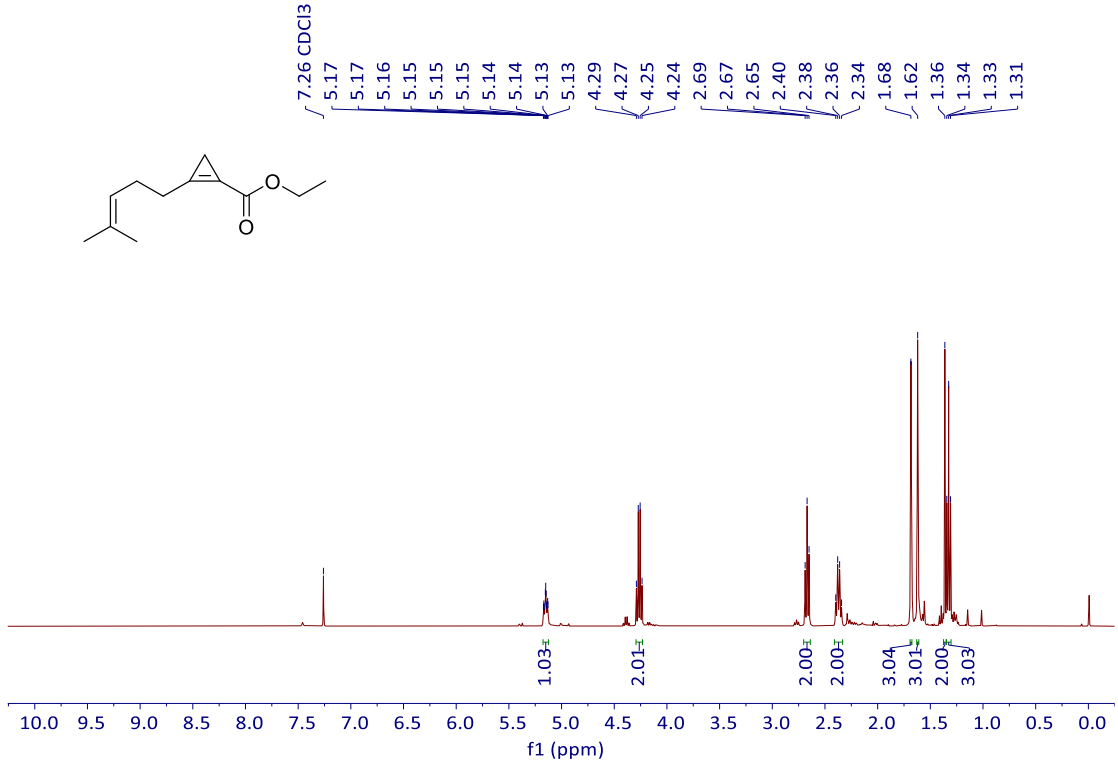

$^{13}$C NMR of **2q** (100 Hz, $CDCl_3$)



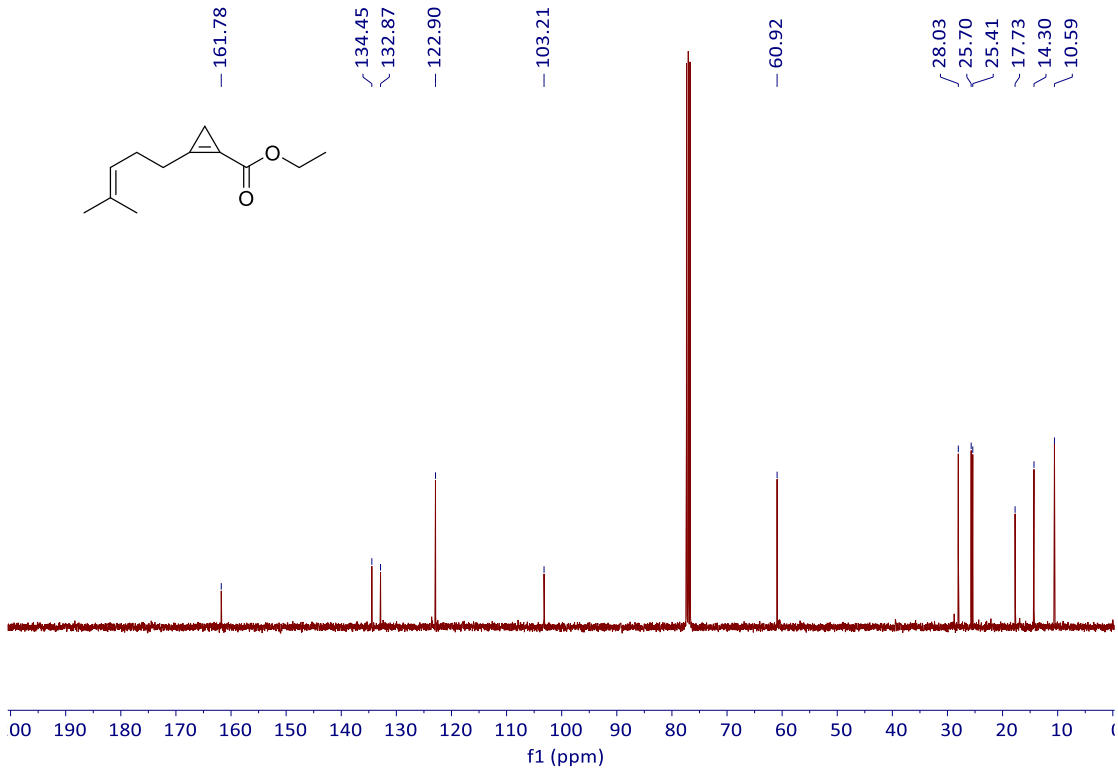

$^{1}$H NMR of **2r** (400 Hz, $CDCl_3$)



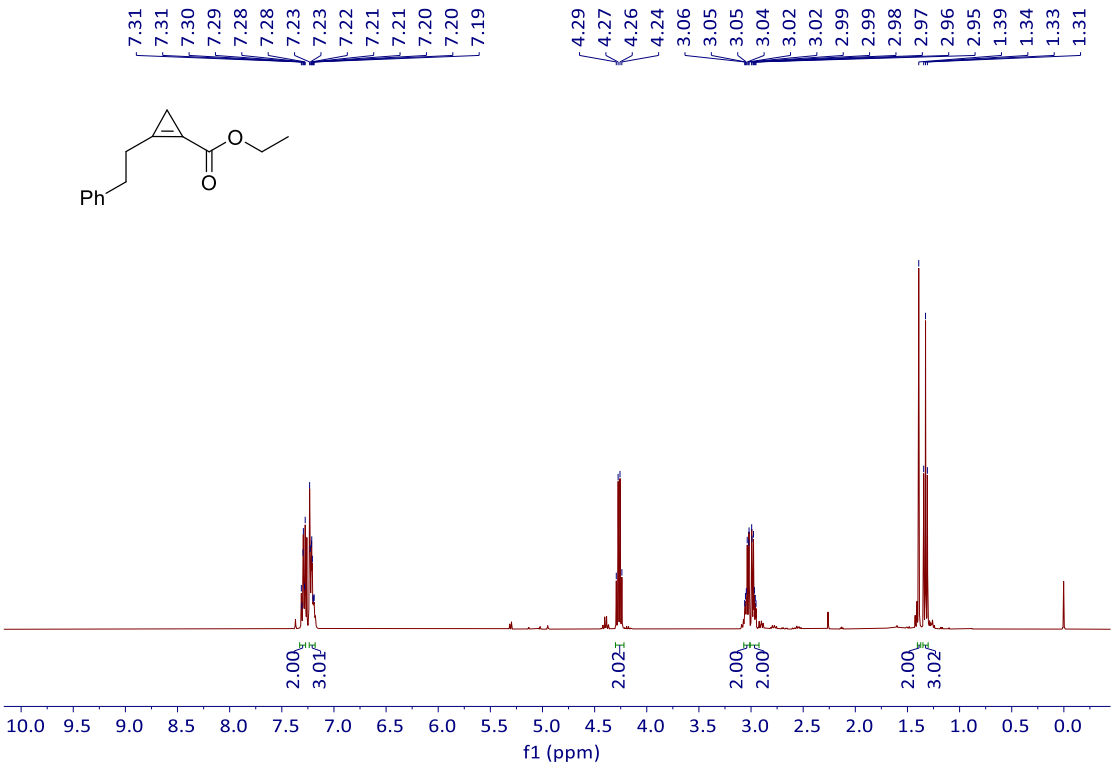

$^{13}$C NMR of **2r** (100 Hz, $CDCl_3$)



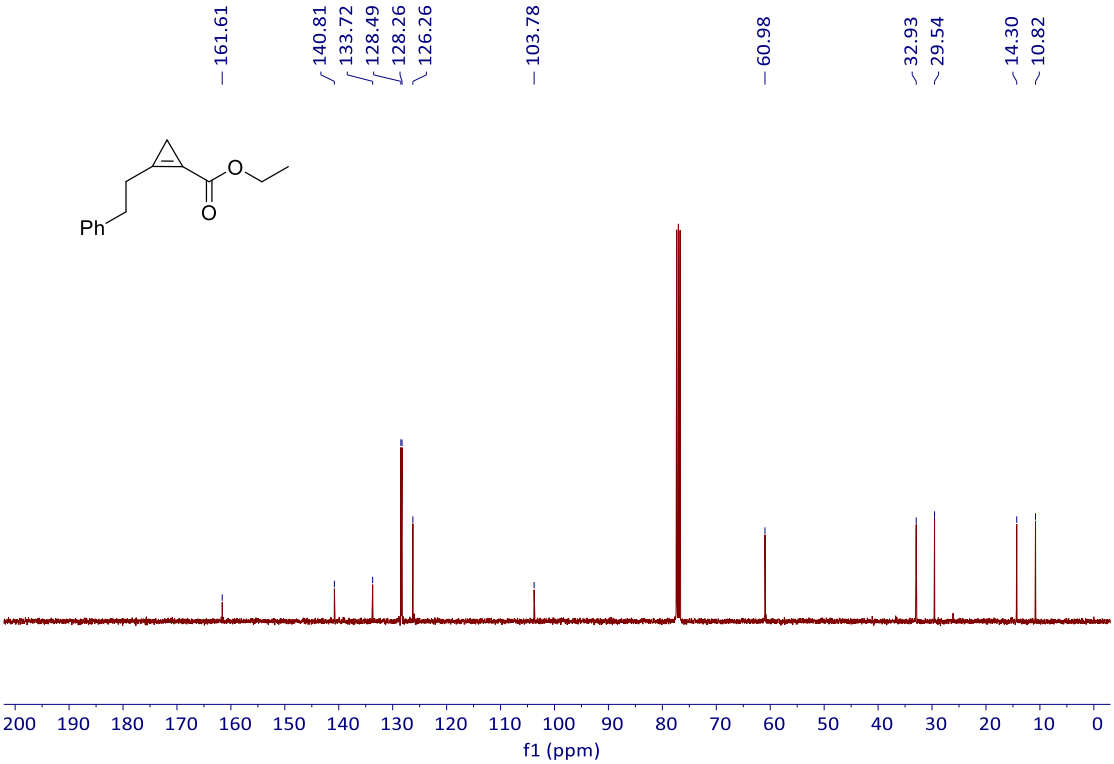

$^{1}$H NMR of **2s** (400 Hz, $CDCl_3$)



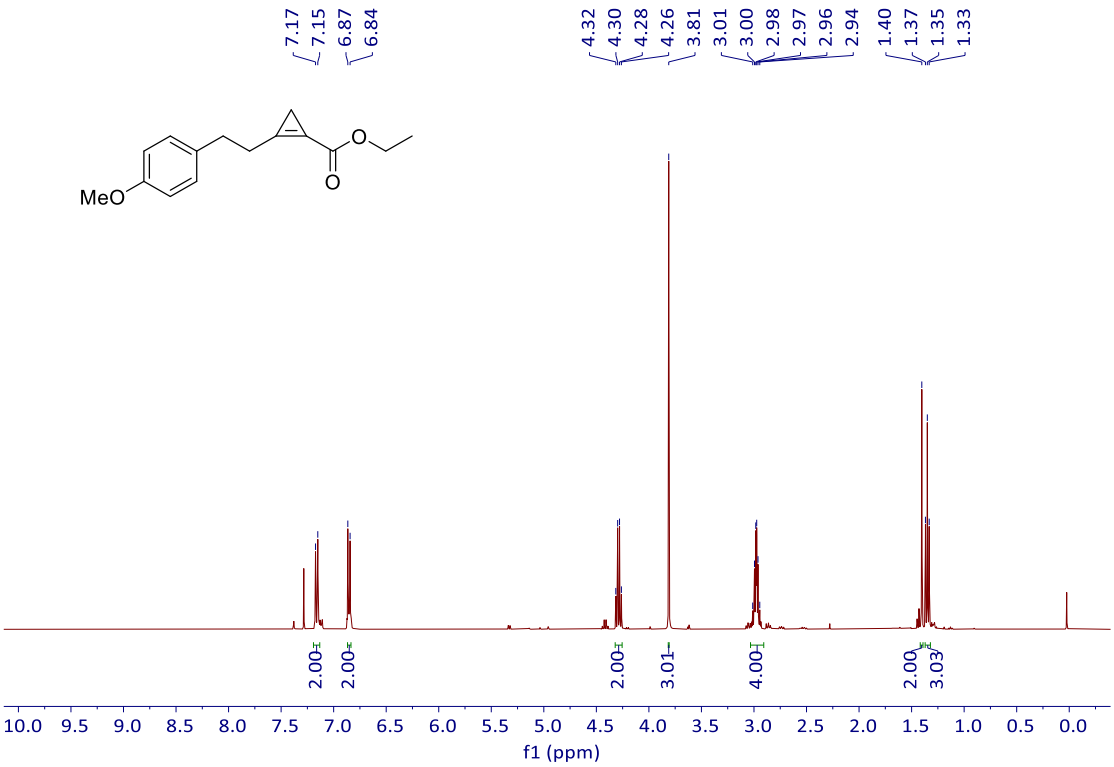

$^{13}$C NMR of **2s** (100 Hz, $CDCl_3$)



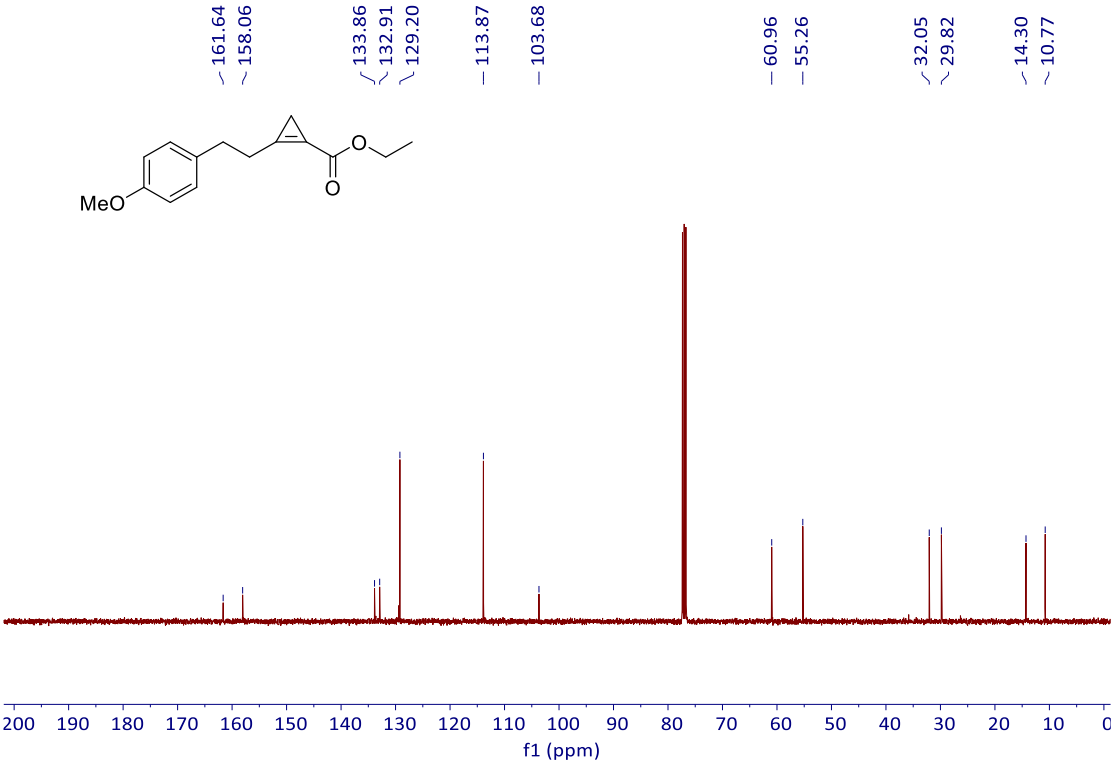

$^{1}$H NMR of **2t** (400 Hz, $CDCl_3$)



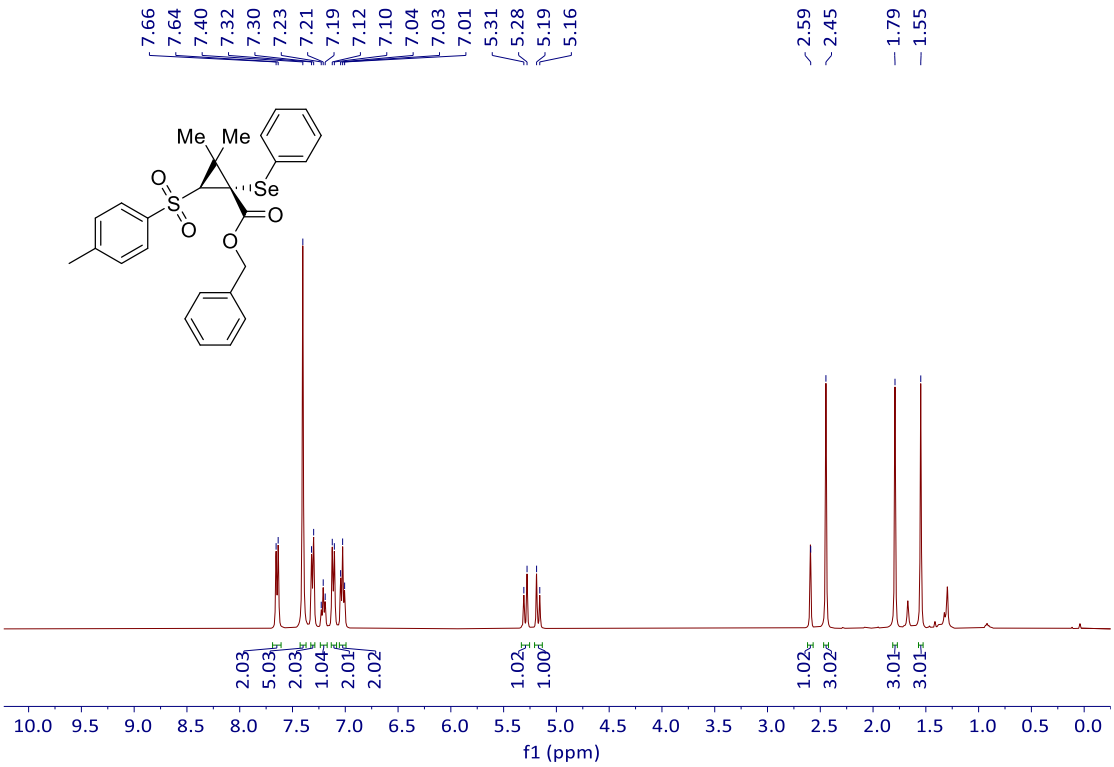

$^{13}$C NMR of **2t** (100 Hz, $CDCl_3$)



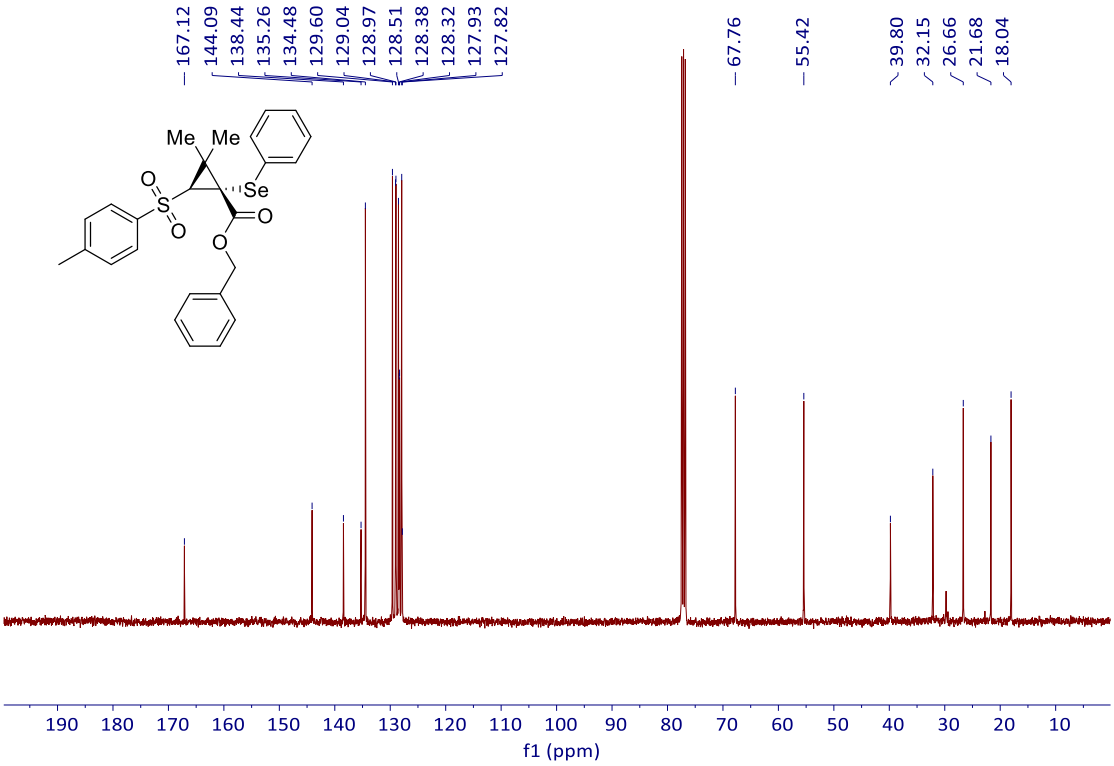

$^{1}$H NMR of **2u** (400 Hz, $CDCl_3$)



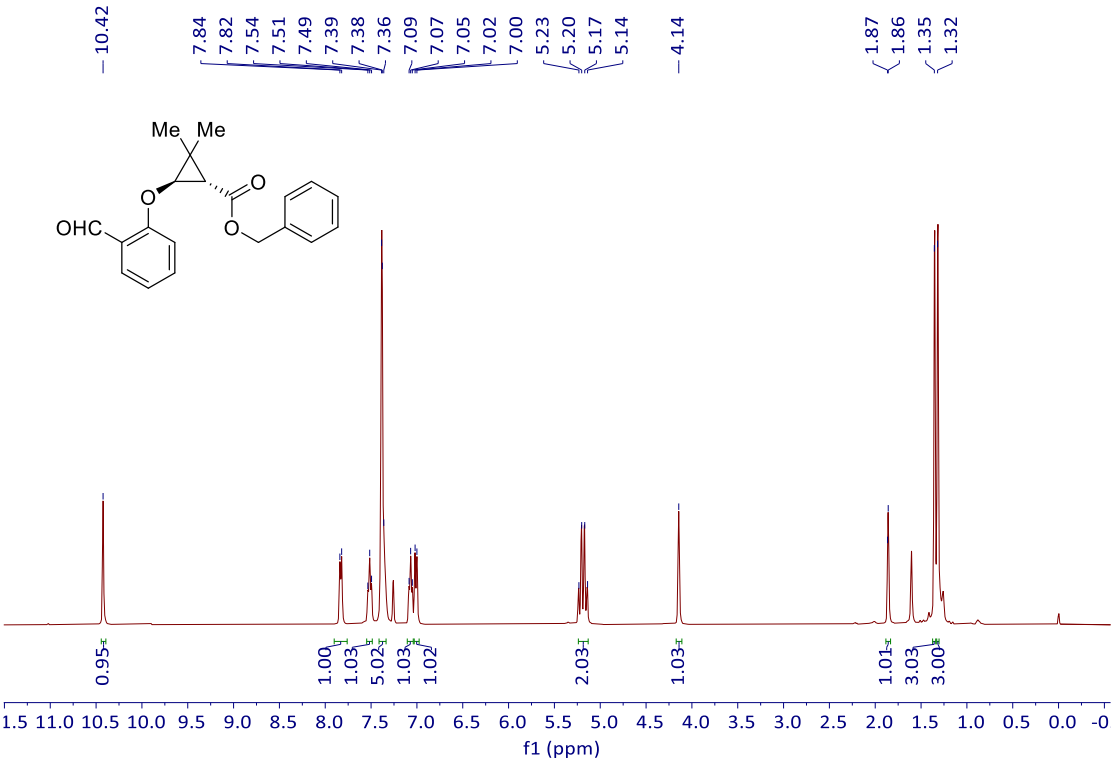

$^{13}$C NMR of **2u** (100 Hz, $CDCl_3$)



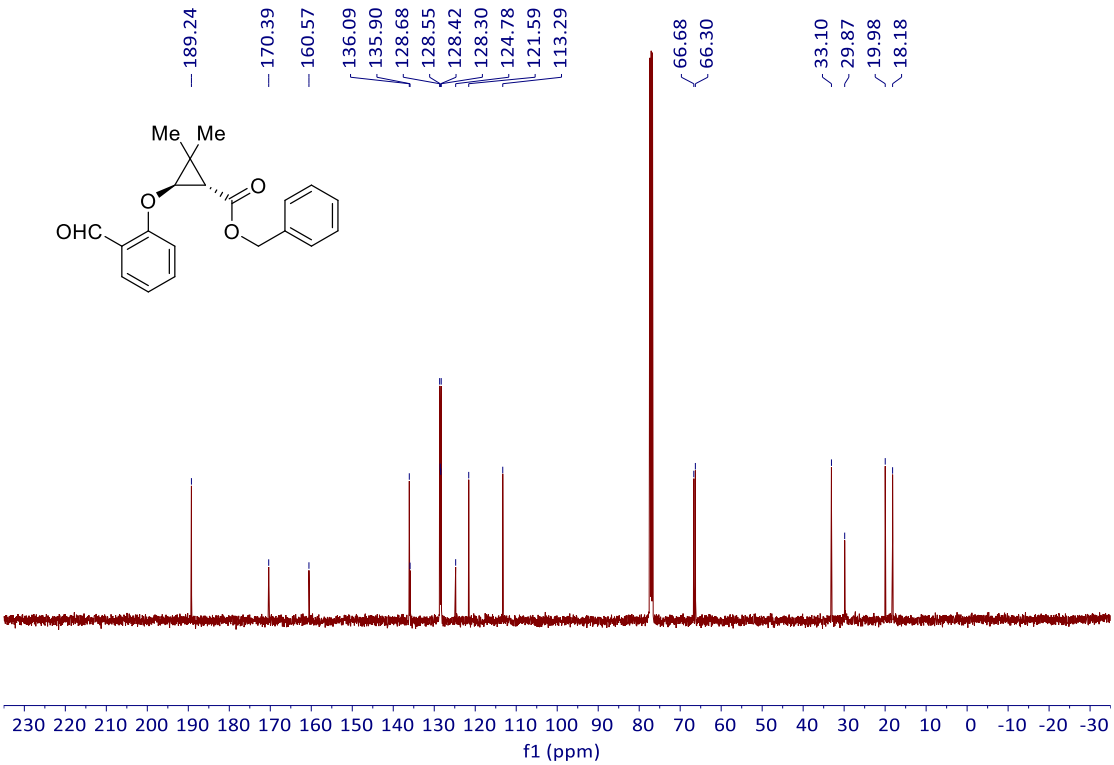

$^{1}$H NMR of **3** (400 Hz, $CDCl_3$)



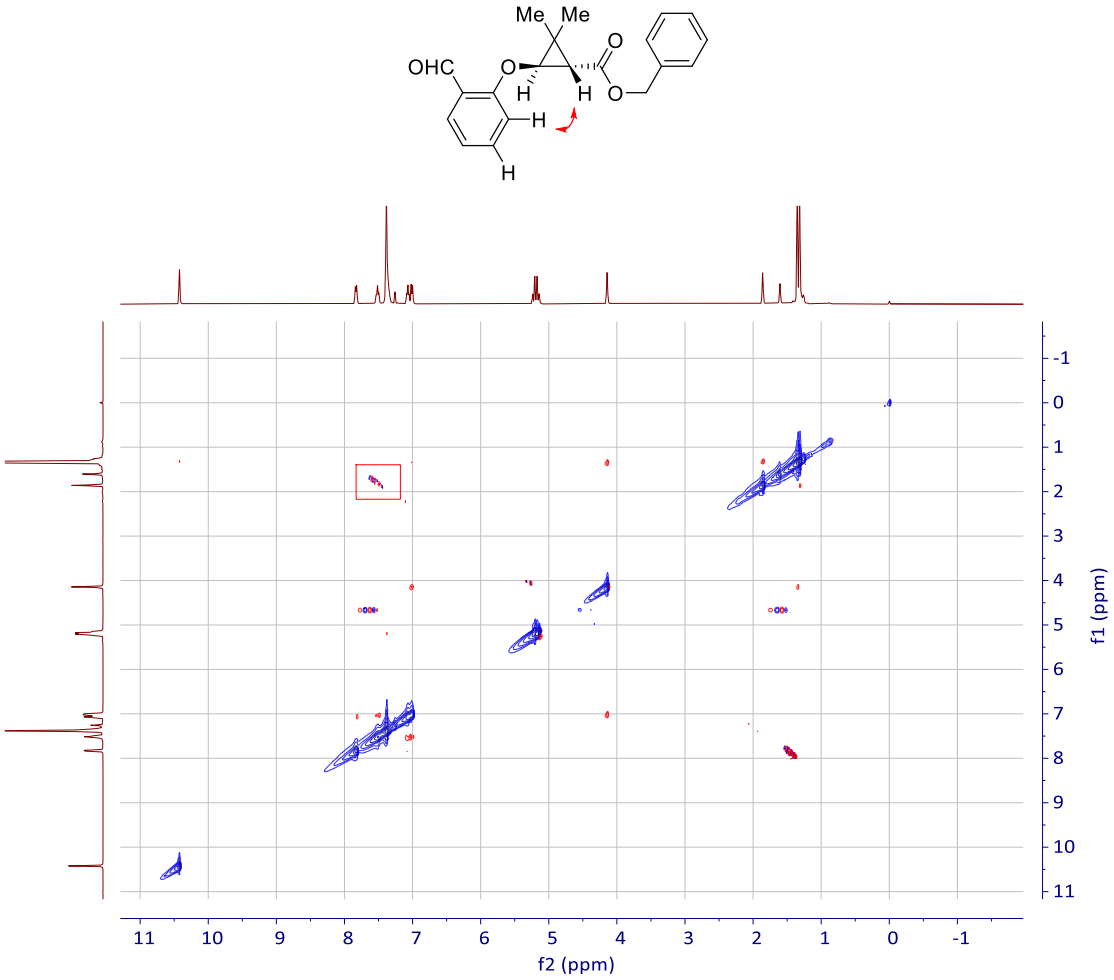

$^{13}$C NMR of **3** (100 Hz, $CDCl_3$)




$^{1}$H NMR of **4** (400 Hz, $CDCl_3$)




$^{13}$C NMR of **4** (100 Hz, $CDCl_3$)




NOESY of **4**